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SCIENCE
NEWS

EDITED BY ARCHIE AND NAN CLOW

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INFRA-RED SPECTROSCOPY

J. E. PAGE

THE development of chemistry and biology during the last twenty years has been profoundly affected by the introduction and wide application of physical methods of analysis, such as chromatography, polarography, procedures involving radio-active and stable isotopes, and visible, ultra-violet, and infra-red spectroscopy. These new physical techniques have increased the tempo of research and have led to the solution of problems that either could not have been undertaken or would have taken very much longer to solve by the older chemical methods.

Infra-red spectroscopy is prominent among these new physical methods. It is one of the most powerful tools available today for the rapid identification and measurement of an organic compound. The recent development of sturdy and reliable record-ing infra-red spectrophotometers has led to a degree of imme-diate and continuous analytical control of complicated chemical syntheses that would have been unthinkable fifteen years ago.

In this article, we shall first find out what is meant by the infra-red spectrum of a compound and then, after a short dis-cussion of the origin of infra-red absorption spectra, we shall see how such spectra are obtained with modern recording instru-ments, how infra-red spectroscopy helps the modern organic chemist to establish the identity of complex substances, how it is used for the quantitative analysis of mixtures of organic com-pounds, and, finally, how it can help to reveal the structure of new and unknown substances.

THE NATURE OF AN INFRA-RED SPECTRUM

Spectroscopy has travelled a long way since Sir Isaac Newton, in 1666, intercepted with a glass prism a beam of sunlight shining into a darkened room and saw a band of colours, the solar

spectrum, on the wall. But it was not until 1800 that Sir William Herschel moved a sensitive thermometer along a similar spectrum of the sun and found that the temperature reached a maximum at a point some distance beyond the red end of the spectrum. He thus demonstrated the existence of heat rays that do not excite the sensation of visible light. At first these new heat or 'infra-red' rays were believed to be fundamentally different from light rays, but by 1840 the identity of the two was generally accepted.

Today, it is recognized that X-rays, ultra-violet, visible, and infra-red radiation, and radio waves are similar in nature and that, as waves, they are capable of reflection, refraction, and interference. The distance between the crests of a wave is known as the wave-length, the number of waves in one centimetre (cm) as the wave-number, and the number of waves that pass a given point in one second as the frequency. Thus a wave-length of 1 cm corresponds with a wave-number of 1 wave per cm, i.e., 1 cm^{-1}; a wave-length of 0·001 cm (100,000 Ångstroms, 10 microns, or 10μ) corresponds with a wave-number of 1000 cm^{-1}.

Visible light is contained within a relatively narrow wave-length region from about $0·40\mu$ in the violet to about $0·70\mu$ in the red part of the spectrum. The infra-red region includes radiations of wave-length just longer than those of red light and extends to the borders of the micro-wave region. The range of the various spectral regions is shown diagrammatically in Figure 1. The part of the infra-red region that is of interest to the chemist lies between 2·5 and 25μ, i.e., between 4000 and 400 cm^{-1}; the region between this and the visible, 0·7 to $2·5\mu$, is called the overtone or near infra-red and that beyond 25μ is spoken of as the far infra-red region. (See Fig. 1, page 10.)

A graph of changes in the intensity of light or infra-red rays plotted against wave-length or wave-number constitutes a spectrum. The position of an intensity maximum or minimum in a spectrum may be given by either the wave-length or the wave-number of the radiation. In infra-red measurements, the frequency unit, wave-number, is to be preferred; it is more closely

allied to the vibration frequency of a molecule than is wavelength. Furthermore, wave-number is readily comparable with Raman displacements, which are also related to molecular vibrations.

Infra-red spectra are of two kinds, emission and absorption. The former are obtained by the spectroscopic analysis of rays emitted by a hot body, and the latter by introducing an absorbing medium between the hot source emitting continuous radiation and the spectrometer. The absorbing medium removes from the spectrum of the source certain wave-lengths, so that the resulting spectrum has a series of absorption peaks or absorption bands. Since infra-red emission spectra are difficult to obtain and have attracted less attention than absorption spectra, we will restrict our study to absorption spectra.

The graphical plotting of an absorption spectrum involves finding both the position and the intensity of absorption bands. This is done by a spectrophotometer.

THE ORIGIN OF AN INFRA-RED SPECTRUM

All molecules consist of atoms joined together by chemical bonds that behave rather like springs. The bonds between the atoms and atomic groups in a molecule are in continuous vibration with respect to one another; each molecule has a set of characteristic frequencies for these vibrations. Molecules with the same atomic structure have the same set of vibration frequencies, but different molecules have different sets of frequencies. These molecular vibrations have the same frequency range as infra-red vibrations.

If an infra-red ray with the same vibration frequency as one of those characteristic of the molecule being studied passes near that molecule, the ray may excite a sympathetic vibration in the molecule and lose some of its energy; this would give rise to an absorption band in the infra-red spectrum of the molecule. If, on the other hand, the frequency of the ray differs from those associated with the molecule, no interaction occurs and the ray is transmitted unchanged.

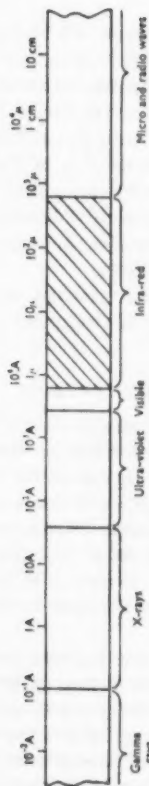The distinctive vibration frequencies, and hence the infra-red
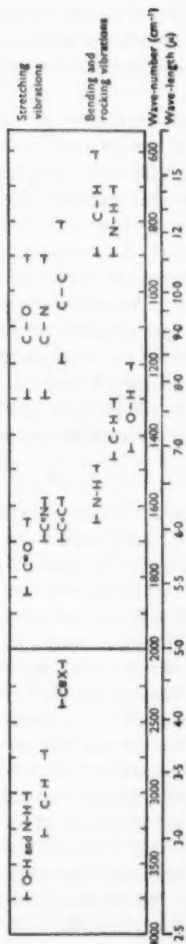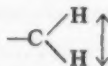
Fig. 1. The electromagnetic spectrum.

Fig. 2. Spectral regions associated with various types of chemical bonds.

absorption spectrum of a molecule, are determined by the masses of the atoms, the spacial geometry, and the strength of the chemical bonds of the molecule.

$$\overset{\longleftrightarrow}{-C-H} \qquad\qquad -C\overset{\displaystyle H \uparrow}{\underset{\displaystyle H \downarrow}{\Big\langle}}$$

1. Carbon-hydrogen stretching vibration.

2. Carbon-hydrogen bending vibration.

The fundamental vibrations of the bonds in a molecule can be divided into two classes, stretching vibrations (1), in which a periodic change in bond length occurs, and bending vibrations (2), which involve a periodic change in the bond angle. The frequencies of the absorption bands associated with the stretching and bending of various kinds of chemical bond differ, and it is possible to assign to each type of bond occurring in an organic compound a definite spectral region. Since more energy is normally needed to change the length of a bond than to change the bond angle, absorption bands associated with stretching vibrations tend, as is shown in Figure 2, to occur at higher frequencies than those for bending vibrations.

Simple gas molecules, such as hydrogen chloride, can vibrate not only along the line joining the atoms, but can also rotate about an axis at right angles to this line. This rotation of the molecule gives rise to a complex pattern of closely spaced absorption bands, the vibration-rotation spectrum. The spacings between the rotation lines in the spectra of large molecules are too small to be observed.

Molecules vibrate not only according to their bond frequencies, but also at overtones of these frequencies. Further, when one bond vibrates the rest of the molecule is involved and the resulting frequencies are characteristic of the complete molecule. The absorption bands appearing between 4000 and 1450 cm^{-1} are associated with relatively simple stretching vibrations and can be empirically correlated with, and used to identify, particular chemical bonds and atomic groupings. Many bands between 1450 and 650 cm^{-1} can also be used in this way, but, in general, the bands in this region are more complex and

are specific for the particular molecule; they provide a unique 'finger-print' of the molecule that is invaluable for its identification. The region between 1450 and 650 cm^{-1} is accordingly termed the finger-print region.

INFRA-RED SPECTROPHOTOMETERS

A modern infra-red spectrophotometer has the same basic components as the original apparatus used by Sir William Herschel in 1800, namely, a hot source emitting infra-red rays, a prism or diffraction grating for dispersing the rays, and a temperature-sensitive device for measuring the radiation. Nevertheless, progress in developing suitable instruments has, until recently, been slow.

In 1903, W. W. Coblentz, an American physicist, constructed a manual instrument for plotting absorption spectra, with which he was able to demonstrate the potential value of infra-red spectroscopy. However, the operation of Coblentz's spectrophotometer was exceedingly laborious and his pioneer work was largely ignored for thirty years. To obtain a single spectrum it was necessary to observe several hundred galvanometer readings and to plot the readings by hand.

During the Second World War there was a big revival of interest in infra-red spectroscopy. H. W. Thompson at Oxford and G. B. B. M. Sutherland at Cambridge started a systematic survey of the spectra of organic compounds and developed reliable recording spectrophotometers. Since the war, British and American instrument manufacturers have removed the drudgery from infra-red spectroscopy. A high quality spectrum can now be recorded automatically on a paper chart in a few minutes. This advance means that infra-red spectroscopy is no longer a highly specialized research tool, but ensures that it can be used as routine in industrial laboratories.

An infra-red spectrophotometer does not differ in fundamental principles from those used in visible and ultra-violet spectrometry. Nevertheless, since glass and quartz absorb in the infra-red region, the dispersing prism, and any windows through which the infra-red rays pass, must be made from an inorganic

halide salt, such as sodium chloride or potassium bromide, and special surface-coated mirrors used instead of lenses to collimate and focus the rays. A sodium chloride prism is normally employed for the 4000 to 650 cm^{-1} region in which most measurements are conducted; a potassium bromide prism is needed if it is necessary to extend the range to 400 cm^{-1}. The hygroscopic nature of these halide salts make it necessary to protect infra-red equipment from high humidity conditions.

Improved resolution can be obtained either by passing the rays through the same prism more than once, as in the so-called 'double-pass' spectrometer, or by replacing the prism by a diffraction grating. The introduction of commercial grating spectrometers has been aided by Sir Thomas Merton's work in devising simpler methods for ruling and reproducing diffraction gratings.

The source of infra-red radiation in a spectrometer is usually either a silicon-carbide rod, called a Globar, or a Nernst filament made from a mixture of cerium, thorium, and zirconium oxides; the source is heated electrically to about 1500° C. In a single-beam spectrometer, the rays pass through the sample under examination, undergo dispersion in the prism and are, finally, measured either by a sensitive thermocouple or by a bolometer. The thermocouple current is amplified electronically, and the corresponding absorption intensity is plotted automatically, on a paper chart, against wave-length or wave-number.

Unfortunately, the spectrum recorded by a single-beam instrument is marred by a complicated series of absorption bands caused by atmospheric water vapour and carbon dioxide. These bands are superimposed on those for the compound under examination and frequently make it almost impossible to measure those for the compound. The effect of atmospheric and solvent absorption can be eliminated automatically by using a double-beam spectrophotometer; these instruments are employed in most laboratories today.

In a double-beam instrument, radiation from a single source is divided into two equivalent beams; one beam passes through

the sample and the other through a reference substance, such as air or an equivalent thickness of solvent. The intensity of the beam that passes through the sample is equalized automatically with that of the reference beam by a variable aperture device. The effective aperture for photometric balance provides a measure of percentage absorption, which can be plotted, on a paper chart, against wave-length.

Fig. 3. Optical system of the Infracord spectrophotometer. (*Courtesy of Perkin-Elmer Ltd.*)

The optical lay-out of a typical double-beam spectrophotometer is shown in Figure 3. Infra-red radiation from the source is split into two separate beams, the sample and the reference beam, by the plane mirror and the two toroid mirrors. Toroid mirror 1 focuses the sample beam through the sample on to the 100 per cent transmission comb, while toroid mirror 2 focuses the reference beam on to the optical wedge. The sample is placed

just in front of the 100 per cent comb. The sample and reference beams after passing through the 100 per cent comb and optical wedge, respectively, are recombined by the semi-circular sector mirror, which rotates at 13 revolutions per second. The sector mirror is mounted so that it alternatively reflects the reference beam and passes the sample beam. Both beams then follow the same path through the rest of the spectrometer. They are focused by toroid mirror 3, and reflected by the plane mirrors on to the entrance slit of the monochromator. On emerging from the entrance slit, the beams diverge until the paraboloid mirror reflects them as parallel rays on to the sodium chloride prism. The rays are dispersed by the prism into their component wavelengths and are then reflected by the Littrow mirror back through the prism, where they are further dispersed. The dispersed rays are focused by the paraboloid mirror to form a spectrum across the exit slit. The selected wave-length that passes through the exit slit strikes the ellipsoid mirror and is focused on to the thermocouple.

If the intensity of the sample and reference beam is the same, the thermocouple produces a direct current voltage, which is not amplified by the alternating current amplifier of the spectrometer. If, however, the sample absorbs infra-red radiation, the intensity of the sample beam is reduced but that of the reference beam is unchanged. A composite beam of alternating intensity is formed which strikes the thermocouple; it is converted to an alternating current voltage and amplified by the 13-cycle amplifier. The amplified signal drives a servo motor, which in turn moves the optical wedge either in or out of the reference beam to equalize the beam intensities. The pen of a recorder is coupled directly to the optical wedge. As the wave-length setting of the spectrometer changes, the position of the wedge changes and the pen traces on a paper chart the variations in optical transmission of the sample.

Three British commercial infra-red spectrophotometers are illustrated in Insets 9, 10, and 11.

Samples for infra-red examination may be studied either as gases, liquids, or solids. About 2 to 5 mg of either a solid or a

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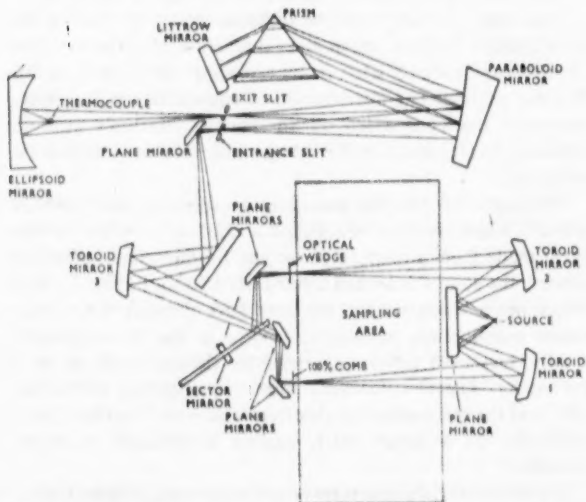

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Samples for infra-red examination may be studied either as gases, liquids, or solids. About 2 to 5 mg of either a solid or a

liquid are normally needed for a measurement, but by using special techniques reliable spectra can be obtained on samples as small as 0·025 mg. This is important for special investigations when it is difficult to obtain larger specimens.

Gases and liquids are examined in cells with either sodium chloride or potassium bromide windows. Liquid cells range in thickness from 0·02 to 1·0 mm and gas cells from 2 cm to 40 metres. The latter were devised to help identify atmospheric contaminants during air-pollution studies in Los Angeles; the rays are reflected back and fore, forty times, through a 50 cm cell.

Solids are examined as thin films, as mulls with a mineral oil such as Nujol, or as pressed discs with halide salts. Powders cannot be studied directly; they tend to scatter rather than transmit infra-red rays. If, however, the powder is suspended in, or mulled with, Nujol and the mull smeared as a thin film between two sodium chloride plates, light scattering is reduced and good absorption spectra are obtained. In the pressed halide disc method, the powder is intimately mixed with a finely powdered halide salt, such as potassium bromide, and the mixture compressed in a vacuum, at a pressure of about 60 tons per square inch, in a special die. A transparent disc is formed, which can be mounted in the spectrometer.

For quantitative measurements, solids must be handled as solutions of known concentration in solvents that transmit infra-red rays. Unfortunately, few solvents are reasonably transparent to infra-red radiation; carbon disulphide, carbon tetrachloride, bromoform, and chloroform are the most satisfactory and the most widely used. Light and heavy water absorb too strongly to be of much value. Nevertheless, by using thin cells (about 0·02 mm) with calcium or barium fluoride windows, useful measurements can, sometimes, be made on strong aqueous solutions.

APPLICATIONS OF INFRA-RED SPECTROSCOPY

The applications of infra-red spectroscopy in chemistry are of three kinds: (*a*) identification of individual substances,

(b) quantitative analysis, and (c) elucidation of the structure of unknown substances.

In modern multistage organic syntheses, it is becoming customary to obtain an infra-red spectrum after each chemical reaction; this spectrum shows whether, and how much of, the anticipated product has been formed and gives a prompt warning if the reaction has not taken the expected course. A spectrum also provides a convenient method for deciding whether a purification has been effective. In skilled hands, infra-red spectroscopy can be applied to new, hitherto unknown, compounds almost as well as to those for which reference spectra are available.

Identification of individual substances

The identification of individual substances by comparison of their spectra with those of known substances makes use of the concept that the infra-red spectrum of an organic compound is unique. A small change in chemical constitution can produce a surprisingly big change in the spectrum. These changes are usually greatest in the fingerprint region between 1450 and 650 cm^{-1}. A comparison of infra-red spectra is often the most convincing way of establishing the identity of two complex substances. It is not always necessary, as for a mixed melting-point, to have a specimen of the known substance on hand; a suitable reference spectrum of the known substance can be used for the comparison.

When comparing spectra, it is important to compare spectra of substances in the same physical state, or dissolved in the same solvent. There are often small, but significant, changes in the spectrum of a compound when its physical state is altered or different solvents are used; both band positions and band intensities may vary. Special care is needed if the spectra of solids are being compared, since, although identity of spectra is good evidence that the two solids are chemically the same, the converse is not always true: the infra-red spectrum of a solid is dependent on crystal structure and crystal orientation. If a substance can crystallize in several different forms, i.e., is poly-

morphic, these different forms will yield identical spectra in solution, but may give different spectra in the solid state. This behaviour provides a convenient test for polymorphism.

In order to facilitate comparisons of spectra, catalogues listing reference spectra for several thousand pure compounds have been published. Reference spectra have also been printed on edge-punched and on machine-sorted I.B.M. cards. The cards are punched with holes that correspond with the frequencies of the stronger bands in the spectrum printed on the card; by sorting the cards for the chief bands in the spectrum of an unknown substance it should be possible to recover, if known, the appropriate reference spectrum and so identify the unknown substance.

Quantitative analysis

The application of infra-red spectroscopy in quantitative analysis depends on the facts that in a mixture of compounds that do not interact the absorption spectrum of the mixture is the sum of the spectra of the individual components and that the intensity of the absorption band associated with any component is proportional to the concentration of that component (see Figure 4). The amount of any substance in a solution can be determined by comparing the height of an absorption band characteristic of the substance with that of the same band for a solution containing a known amount of the substance. Usually a series of solutions containing known amounts of the substance to be determined are made up and the spectrum of each solution recorded. A calibration curve of percentage absorption against concentration is prepared and the concentration of the unknown solution read off. If the unknown solution shows bands that cannot be attributed to any known component, we have direct evidence of an unsuspected impurity; these bands can be used to help identify the impurity.

Infra-red spectroscopy is of special value for the analysis of isomers and closely related compounds that cannot easily be distinguished by other methods. The infra-red procedure employed for the analytical control of the heavy water used as a
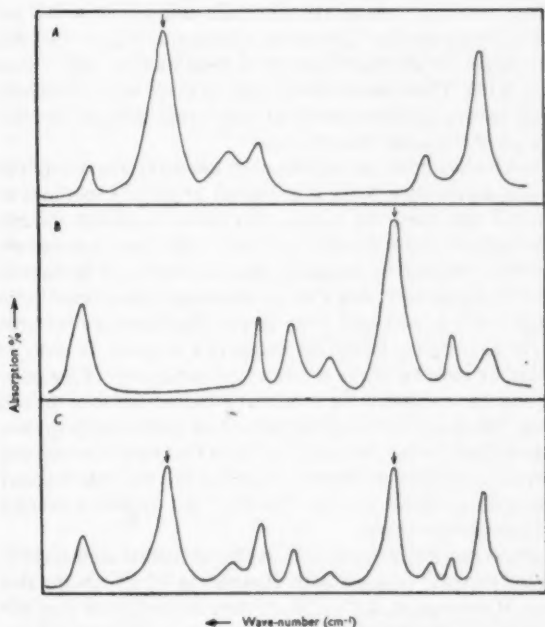
Fig. 4. Infra-red absorption spectrum of a mixture. (a) Absorption spectrum of compound A. (b) Absorption spectrum of compound B. (c) Absorption spectrum of mixture of A and B.

moderator in certain reactors at the Atomic Energy Research Establishment, Harwell, is a good example of quantitative infra-red spectroscopy. If the heavy water in an operating reactor is diluted with light water a loss of power results. Density and mass spectrometric methods, which have been used previously for the determination of heavy water, are time-consuming and are less satisfactory for continuous plant-monitoring. Heavy water has an oxygen-deuterium stretching band at 2513 cm^{-1}

$(3\cdot98\mu)$, which is used to measure trace amounts (0 to 0·8 per cent) of heavy water in light water; a band at 3394 cm^{-1} $(2\cdot946\mu)$ is employed for the determination of light water in nearly pure heavy water. These measurements can be made with a relatively simple grating spectrometer fitted with a lead sulphide detector in place of the usual thermocouple.

Quantitative infra-red spectroscopy has many applications in the plastics industry. Since it is difficult to prepare solutions of synthetic polymers, the samples are often examined directly either as films or as a thin sheet of known thickness. Satisfactory results are obtained by measuring the overtone bands in the near infra-red region and using a simple spectrophotometer similar to that devised for the heavy water assays. The technique has been used to estimate the molecular weight of a polymer. In order to do this, we must know the nature of the end-groups of the polymer and find an absorption band that is characteristic of the end group. The molecular weight of polyethers, such as polyethylene oxide and polyoxycyclobutane, in which the chain is terminated by hydroxyl groups, has been measured in this way; the intensity of the hydroxyl band at about 4760 cm^{-1} $(2\cdot1\ \mu)$ gives a measure of the molecular weight.

Certain polymerizations, such as that of methyl methacrylate to give Perspex, proceed with elimination of an unsaturated group of the type, $R_1R_2C=CH_2$. If the polymerization does not go to completion some of the monomer containing the unsaturated group will be left in the polymer. The course of such reactions can be followed by observing the changes in intensity of the band at about 5880 cm^{-1} $(1\cdot7\ \mu)$ associated with the $R_1R_2C=CH_2$ group.

Elucidation of the structure of unknown substances

The most common, and undoubtedly the most important, application of infra-red spectroscopy is to the elucidation of the chemical structure of unknown organic substances. A cursory inspection of a spectrum by an experienced eye will often reveal information on atomic groupings, such as hydroxyls and carbonyls, that the substance contains, information that might

require several weeks work to obtain by ordinary chemical methods.

This application depends on the observation that most atomic groupings have characteristic vibration frequencies in the infra-red region. Hydroxyl (O—H), carbon-hydrogen (C—H), carbonyl (C=O), and carbon-chlorine (C—Cl) bonds absorb at about 3600, 3000, 1710, and 750 cm^{-1}, respectively; the exact position of the band, which depends on the molecular environment of the linkage, gives more detailed information about the nature of the linkage. The absorption frequency of a carbonyl bond appears within different well-established ranges depending on the nature of the group of which it forms a part; for example, the carbonyl of an open-chain ketone, —CH$_2$.CO.CH$_2$—, absorbs at about 1715 cm^{-1}, of a conjugated ketone, —CO.CH= CH—, at about 1670 cm^{-1}, and of an acetate, CH$_3$CO.OR, at about 1735 cm^{-1}. We can use the band intensity to ascertain the number of groups of each type present in a given compound. Thus the intensity of the acetate carbonyl band for a compound containing two acetate groups is twice that for a similar compound containing one acetate group.

An infra-red spectrum can also provide information on the spacial arrangement of the atoms in a molecule. The *cis* and *trans* forms of a compound can be distinguished, as can *ortho, meta,* and *para* isomers.

This is not the place to give a detailed list of the characteristic group frequencies for each type of atomic grouping. In 1950, N. B. Colthup compiled a list of the frequencies for the commoner organic groups. The correlations are discussed in greater detail in L. J. Bellamy's and in R. N. Jones and C. Sandorfy's excellent monographs on the infra-red spectra of complex molecules; these should be consulted for further information.

As examples of the value of infra-red spectroscopy in chemical structure problems, we will consider the spectra of two pairs of isomers, namely, benzyl acetate and ethyl benzoate, and 2α-chlorocholestan-3β-ol and 2β-chlorocholestan-3α-ol.

Although benzyl acetate and ethyl benzoate have the same empirical formula, C$_9$H$_{10}$O$_2$, and are therefore isometric, their

infra-red spectra, which are shown in Figures 5a and 5b, respectively, are quite different. The absence from both spectra of strong bands between 3600 and 3200 cm^{-1} shows that the compounds do not contain hydroxyl (O—H) and nitrogen-hydrogen (N—H) groups. The strong bands between 3000 and 2850 cm^{-1}
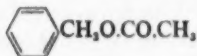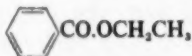
Benzyl acetate.   Ethyl benzoate
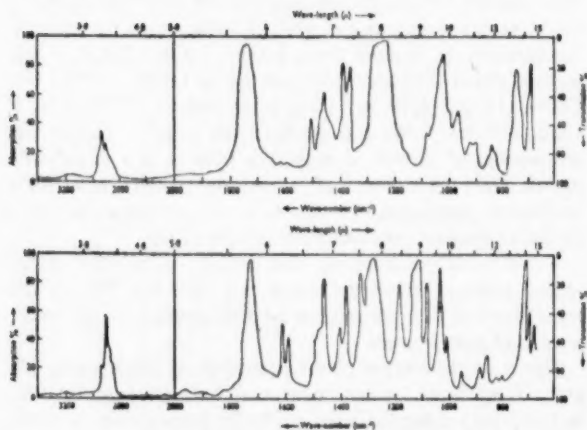
Fig. 5a. Infra-red spectrum of benzyl acetate.
Fig. 5b. Infra-red spectrum of ethyl benzoate.

are assigned to various carbon-hydrogen (C—H) linkages. The bands at 1740 and at 1227 and 1027 cm^{-1} in Figure 5a are associated with the carbonyl and carbon-oxygen linkages, respectively, of the acetate group. Similarly, the bands at 1725 and at 1277 and 1108 cm^{-1} in Figure 5b are assigned to the carbonyl and carbon-oxygen bonds, respectively, of the benzoate group. The pattern of the bands in the 1600 and 700 cm^{-1} region of

both spectra confirms the presence in both compounds of a mono-substituted benzene ring. The spectra can be used in this way to distinguish between the two isomers and to help assign the correct structures.
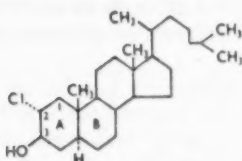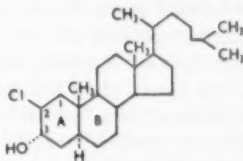
2α-Chlorocholestan-3β-ol.   2β-Chlorocholestan-3α-ol.
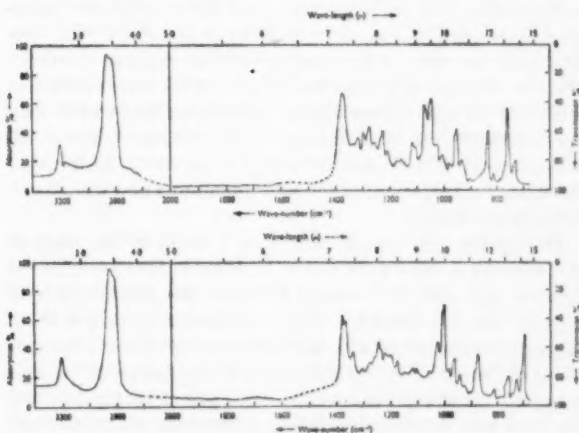
Fig. 6a. Infra-red spectrum of carbon disulphide solution of 2α-chlorocholestan-3β-ol.
Fig. 6b. Infra-red spectrum of carbon disulphide solution of 2β-chlorocholestan-3α-ol.

The two steroids, whose infra-red spectra are reproduced in Figures 6a and 6b, have the same empirical formula, $C_{27}H_{47}OCl$, and are identical in every way except in the spacial arrangement

of the chlorine and hydroxyl substituents. In 2α-chlorocholestan-3β-ol, both substituents are in the plane of ring A and are said to be equatorial, while in 2β-chlorocholestan-3α-ol, they are both approximately perpendicular to the plane of ring A and are axial. Figures 6*a* and 6*b* show that although the chemical difference between the two steroids is small, the difference between the spectra is immense.

Both spectra show bands in the 3600 cm^{-1} region indicating the presence of a hydroxyl group. The hydroxyl band for 2α-chlorocholestan-3β-ol at 3600 cm^{-1} is 20 cm^{-1} lower than that for 2β-chlorocholestan-3α-ol, 3620 cm^{-1}; this shift is of the expected amount for equatorial and axial hydroxyl groups, respectively. The carbon-oxygen and carbon-chlorine bands also show small relative shifts that can be correlated with their spacial arrangement. The equatorial carbon-oxygen and carbon-chlorine linkages in 2α-chlorocholestan-3β-ol, which absorb at 1053 and 755 cm^{-1}, respectively, have higher frequencies than the corresponding axial linkages in 2β-chlorocholestan-3α-ol, which absorb at 1006 and 693 cm^{-1}, respectively. In this way the spacial arrangement of the substituents in a new steroid can often be established.

During the past decade, largely as a result of the work of K. Dobriner in New York and R. N. Jones in Ottawa, infra-red spectroscopy has been widely used for the identification of steroids and has become a routine analytical technique in all laboratories concerned with the isolation, degradation, and synthesis of steroid hormones and vitamins. The spectacular chemical syntheses of cortisone and its more potent analogues could not have been developed so rapidly without the aid of infra-red spectroscopy.

In the field of medical research, infra-red spectroscopy has been used to identify and determine the steroids excreted in the urine under various physiological and pathological conditions. In this work, very complex mixtures are encountered and normal chemical methods cannot be used. Jones and Dobriner overcame these difficulties by using adsorption chromatography in conjunction with infra-red spectroscopy. The steroid mixtures

were split into fractions by chromatography and each fraction submitted to infra-red examination. Individual steroids were identified by comparing their spectra with those of known steroids; the structures of unknown steroids were established from a knowledge of the positions of absorption bands associated with particular chemical bonds and atomic groupings.

Recent developments

Although the frequency ranges of the absorption bands associated with most chemical groups are known, less information is available on the *absolute* intensity of the bands. The measurement of absolute band intensity is not so easy to do in the infra-red as in the ultra-violet and visible spectral regions. Whereas intensity measurements conducted with the same instrument are usually reproducible, measurements on the same sample with different spectrophotometers often show big variations. During the measurement of band intensity, it is assumed that the measurement is undertaken with pure monochromatic radiation. This is never true in practice, but provided that the slit-width of the spectrometer is small compared with the width of the absorption band, the deviation from strict monochromacity does not seriously affect the band intensity. This requirement is satisfied in most ultra-violet spectrophotometers. In an infra-red spectrum, however, the bands are much narrower so that the apparent band intensity varies with slit-width; this difficulty can be overcome either by measuring the area of the absorption band, the so-called integrated absorption intensity, or by using a grating spectrophotometer with a high resolving power.

Recent work has shown that the absolute intensities of the bands for many chemical groupings, like the band positions, depend on the nature of the group and its molecular environment. The intensity values are of particular importance in theoretical studies and can be used to compute the bond polar properties of simple molecules. Absolute intensity measurements should supplement the information obtained from a study of band position and help the chemist to elucidate with greater certainty the structure of unknown substances.

It does not require great boldness to predict that organic chemistry will become increasingly dependent on infra-red spectroscopy. This does not mean that the other physical methods, such as chromatography and other spectroscopic techniques, will be less used. They all have important parts to play and will be assisted, when necessary, by newer physical methods, such as mass spectrometry and nuclear magnetic resonance.

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TOUCHING

S. A. BARNETT

FOR Aristotle, of all the senses touch was the most fundamental. The human sense of touch, he held, is more discriminating than that of other species, and to this can be attributed our intellectual abilities. Nowadays, perhaps, we should be more inclined to relate our intelligence to our manual dexterity; but delicate manipulations themselves depend on the accuracy of the reports we receive from our finger tips. Between the fourth century B.C. and today ideas about the skin senses have undergone many changes, though this aspect of social history does not seem to have been written up. A prominent feature has been the taboo on many kinds of contact between human beings – a system of hardly acknowledged prohibitions linked, in our own time, with restricting phobias and inhibitions about sex: for the most obvious of the emotional aspects of our skin sensations are those connected with love-making.

Yet metaphorical phrases continue, it seems, to reflect emotional truths, as in the expressions 'touching' and 'getting under his skin'. We 'get in touch' with people, and it is now beginning to be conceded, sometimes with reluctance, that 'contact' must be accepted as a transitive verb.

Today there is a new source of ideas on the role of the skin in behaviour. Experiments are being done, and observations made, which suggest that the usual account of the roles of the mammalian skin is notably incomplete. The object of this article is to describe some of this new work, and to propose some speculative applications to man.

THE SKIN SENSES

If you prick your finger or toe lightly, and pay careful attention to what you feel, you may be able to observe that there is a

double sensation: a first and immediate feeling, only slightly painful, and a second and more prolonged one of different quality. The sensory nerve fibres of the skin conduct impulses at different rates: one group reaches the central nervous system ahead of the other and, if the distance travelled is great enough, the two resulting sensations can be distinguished. This effect must be very marked if the hind foot of an elephant is suitably stimulated.

Our knowledge of the different kinds of environmental change that can be detected by the skin is extensive but far from complete. In ordinary language we say that we can feel touch (often through movements of the hairs against sensory nerve endings around their roots), pressure, heat or cold, and pain. Surprisingly, it is the painful sensations that are often conducted by the slow fibres; or, to put the point in objective terms, it is the stimuli that cause immediate withdrawal that produce impulses in these fibres. One might expect that, since the response to these stimuli is withdrawal, the most rapidly conducting fibres would be concerned. Perhaps the low velocity of the impulses ensures a spread of their effect in the brain and so withdrawal to a painful stimulus, even if it affects only a very small area of skin.

Other skin stimuli are sought rather than avoided. Apart from those of touch, which may have profound emotional significance, gentle warmth is welcomed: we (and other mammals) are so equipped that we tend to keep the skin surface over most of the body within a fairly narrowly defined range of temperatures, though this range varies a little according to what we are accustomed to. This temperature sense is localized in the skin in a peculiar way: if the skin is touched with a cold or a hot object of small diameter, such as the head of a nail, the subject will report a sensation of heat or cold only if touched at certain points. Just what sense organs are responsible remains obscure.

The vast number of 'messages' continually leaving the skin pass in bundles of nerve fibres to the central nervous system, and at least those resulting from touch and pressure eventually reach the cerebral cortex. Here there is a substantial area in

which different points correspond to different areas of skin. During an operation on the brain it is sometimes possible to stimulate this area directly: the patient then reports a sensation, perhaps of tingling, in the corresponding peripheral part.

HANDLING AND RESISTANCE TO STRESS

These examples illustrate the sort of information we already have about the skin – information that has got into the text-books. We must now consider a very different type of fact. The first example comes from the work of F. S. Hammet, published in 1921 and 1922. Hammet was studying the influence of the parathyroid glands on calcium metabolism. These glands, lying in the neck very close to the thyroid, can be completely removed by an operation on a laboratory animal such as the rat. The result is an abrupt decline in the level of calcium ion in the blood; this is followed by tetany (muscular spasms), fever, and – as a rule – death during convulsions. In his first set of experiments Hammet had two groups of rats: in one, 79 per cent died from the operation in 48 hours; in the other, only 13 per cent died in the same time. The two groups of rats were of the same strain, and had been identically treated but for one thing: the second, or more robust, group had been regularly handled while being cared for in the laboratory, while the rats of the first group had been left severely alone in their cages.

Hammet published his work in journals read mainly by physiologists, and for a long time his incidental study of the effect of handling was ignored. In any case, it fitted into no existing pattern of ideas or theoretical framework; nor, as we shall see, does it yet fall securely into an established scheme. However, quite recently the subject has been taken up again, and a relationship between handling and resistance to injury (or 'stress') has been confirmed.

The experimental procedure is to take inbred laboratory rats and to divide them into two groups; each group contains the same number of males or females, from the same litters, and so is genetically almost identical; further, with one exception, each group has been reared in identical conditions. The exception is

that the rats of one group are regularly handled, while those of the other (the controls) are left alone. The handling may take the form of being held for ten minutes each day, during which time the animal is stroked. Needless to say, the form of stroking is standardized.

There are now two kinds of rat, 'gentled' and 'non-gentled'. The next stage is to apply some test to both groups. In some Canadian work, the rats were deprived of food and water for sixty hours and then, after an interval of several days, they were deprived again for a longer period. Six rats that had been handled all survived this exceedingly ruthless test, but four that had not been handled died.

There have been comparable results from other, less lethal, procedures. One type of 'stress' is that produced by immobilizing animals by binding them up. Rats were kept in this state for forty-eight hours, and it was found that gentled animals were less affected than the controls. In particular, the non-gentled animals suffered damage to the heart and blood vessels.

It may seem strange that gentling should influence in the same way the response to such different types of adverse conditions. It is however a fact that very diverse noxious agents, such as cold, infection, wounding, and excessive exercise all have certain physiological effects in common. In particular, they all produce an increase in the secretions of the adrenal cortex. The adrenal glands are endocrine organs lying near the kidneys; their outer layers, forming the cortex, secrete hormones which influence a great variety of bodily processes, including the metabolism of both protein and carbohydrate and the distribution of inorganic ions in the tissues. It seems that increased secretion of cortical hormones helps the body to resist many types of unfavourable conditions, or many types of 'stress'. The increase in cortical activity that occurs almost at once on the application of a 'stress' is followed, if the stress continues, by enlargement of the adrenal glands: this is an example of the familiar fact that the more work an organ has to do the more efficient, and often the larger, it becomes.

It is therefore important that, in the work on the effect of

immobilizing rats, it was found that the gentled animals had smaller adrenals at the end of the experiment than the non-gentled. The exact significance of this observation has however not been established. It is rather as though the gentled rats 'take it calmly' when strapped up, while the non-gentled ones become more agitated. This notion, which sounds subjective and anthropomorphic (two adjectives which are terms of abuse in some quarters), has some basis in observed fact. An emotional or excitable rat may be defined, for purposes of experiment, as one that urinates and defecates more than is normal; that 'freezes' when disturbed; and that tends to remain still instead of moving about confidently. It has been shown, for instance by S. Levine and his colleagues, that rats which have not been handled in early life are more emotional, in this sense, than those that have been handled.

WILDNESS AND ANXIETY

The description of an emotional rat applies to tame, laboratory animals – usually the familiar white rat, though some tame rats belong to black, piebald, or other varieties. But emotionality, as defined, has something in common with wildness: wild rats urinate and defecate when disturbed, they tend to keep still under cover when human beings are about, and the confidence with which they move about is easily upset. Taming these creatures is however possible. The common 'brown' rat, *Rattus norvegicus* (the species of which laboratory rats are varieties), can be tamed by daily handling from infancy. This is often regarded as a way of getting the animals accustomed to human beings, but it is clearly more than this: taming depends on *handling*, for the mere presence of an experimenter each day is not enough. It seems, in fact, that taming a wild animal is a very complex process, and studies of the effects of 'gentling' may throw some light on it.

The responses of an animal which have been given the term 'emotional' reflect an activation of the autonomic or involuntary nervous system. The same sort of thing happens in man: we are all familiar with the incontinence which often accompanies

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fear or anxiety. The autonomic nervous system is especially concerned with the mobilization of the body for an emergency. Since the work of W. B. Cannon more than forty years ago, it has been known that in conditions such pain, hunger, fear, and rage the distribution of the blood is altered, blood pressure and heart rate rise, and other changes take place which make the body more ready for violent action. The ability of the body to respond rapidly in this way is obviously important for men in primitive conditions and for wild rats, but less so for city dwellers and not at all for tame rats living a sheltered life in a laboratory. The relationship between wildness and 'emotionality' is therefore not surprising.

The words in which behaviour is described are often those with which we are accustomed to describe our own feelings. 'Emotion' is an obvious example. One kind of unpleasant emotional state of great importance is anxiety. This word has come to be used in medicine to refer to a condition which can be so serious as to be crippling: it is not the reasonable anxiety to which we all are liable before some ordeal, but a state not related to the actual circumstances of the sufferer at the time: it is usually attributed to some unconscious cause and is perhaps due in part to experiences in early life. Anxiety in this sense we know about in others from observing their demeanour and from hearing what they say. But there are accompanying signs that can be measured: for instance the amount of sugar in the blood is increased and the pulse rate and blood pressure rise; the respiratory rate too may be affected. We saw above that such changes are also observed in 'emergencies' such as circumstances that cause pain or fear. In chronic anxiety, it seems, the autonomic nervous system is continually activated to bring about these internal changes.

If we redefine the term 'anxiety' to mean the constellation of measurable bodily effects just mentioned, there is some case for saying that *stroking rats makes them less anxious*. This, perhaps speculative, notion is based partly on the assumption that wildness, emotionality, and anxiety all represent similar internal states. But there are other reasons for believing that gentling

reduces anxiety. Gentled rats are heavier than non-gentled: they not only lay down more fat, but also have larger skeletons. This is not because they eat more food, but because they make better use of the food they do eat. Anxiety in man is often accompanied by a reduction in the efficiency with which the body utilizes food.

All these statements are based on studies of only one species, but there can be little doubt that many other species of mammals, besides rats, are much affected by cutaneous stimulation. This type of responsiveness has, in particular, obviously been much enhanced during the domestication (and taming) of our most intimate animal companions – cats and dogs. There are many semi-wild cats in our cities. It would be interesting to know whether their rather farouche behaviour is to any extent a consequence of their not being stroked.

GENTLING AND LEARNING

So far we have been concerned with the 'emotional' side of behaviour: that is, the internal, especially nervous and hormonal, states that influence the type and intensity of bodily activities. We have not mentioned behaviour that is gradually or suddenly modified in an adaptive way to attain an end: in other words, the learning process has been left out. But this, too, is influenced by gentling.

In some American work laboratory rats were studied in a simple learning situation. They were put in an apparatus called a T-maze. Starting in one arm, they could turn left or right at the end. One of the alternative passages was marked with a light; if they chose that one they were rewarded with food, but if they chose the other they got nothing. Three groups of rats were tested in this situation: one group had had no handling, one had had a little, and the third, comparatively speaking, had been much handled. The differences between the three groups were very clear: the extra-handled rats learned best, and those that had not been handled did worst; that is, they made the most mistakes.

There was also a notable effect of change in the amount of

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handling received. The same rats were used in a test of retention. The question was: how well did they remember what they had learned some time after the original training in the T-maze? Some of those which had not been handled were handled after the first part of the experiment and before the test of memory; that had little effect. But some of the rats accustomed to being handled were left untouched for several days and then retested; and in them, the learning already achieved was severely disrupted. Once the rats were used to handling, breaking it off had a disastrous effect on their ability to carry out a learned performance; in fact, the interrupted rats were worse than those that had never been handled.

These observations show that emotional or motivational factors connected with handling are involved in the effect of handling on learning. It seems likely that the primary effect is, as already suggested, on this aspect of nervous function, but it is not at all clear how improved learning ability comes to be a sort of by-product of better 'nervous tone'. Nor is it evident why cutaneous stimulation should have such an influence on central nervous function. Indeed, the sum of the work done on gentling rats presents such an odd picture that one is naturally inclined to look for means of explaining it all away. Yet there seems no doubt that it is specifically stimulation of the skin by contact that is important. This has been made especially clear by the Canadian psychologist, W. J. McClelland. He subjected white rats to five types of experimental conditions: one group was stroked regularly by hand; a second group was held in a restraining cage and stroked with an artist's brush; a third was held in the hand for a period each day, without stroking; a fourth was subjected only to the restraining cage; and a fifth group was left alone entirely. The members of *both* the first two groups grew better than those of any of the other three.

CUTANEOUS STIMULATION AND SOCIAL SIGNALS

If we accept, then, that these effects of cutaneous stimulation are real, we are left with many unanswered questions, of which one is: what is the biological significance of the effect of con-

tact stimuli? As a beginning, we may turn to observations of social behaviour in wild rats for an answer. Male wild rats are very combative: in particular, they are liable to attack violently any strange male that enters their territory. At the same time, all rats are highly gregarious animals: they live in colonies and sleep huddled together. The impulse for one rat to approach another is very strong: even a male that has been attacked and defeated may approach the victor again and again.

The approach of one rat to another is often marked by specific signals. (It might be said that it is *always* so marked, since olfactory stimuli are always present; but such odours are not readily detected by the human nose and are difficult to study.) An attacking rat chatters its teeth and often adopts a specific threat posture with arched back. By contrast, a non-belligerent rat has 'amicable' signs that involve some form of *contact* with the other rat. The most distinctive is simply crawling under the belly of the second rat; another is grooming it, that is, nibbling gently at its fur. The general effect of this sort of behaviour is to reduce conflict. Social signals of this kind are very widespread among animals. The important thing for the present argument is that these amicable signals in rats depend on cutaneous stimulation: in fact, they resemble stroking. So far as our knowledge goes at present, they fit in rather well with the results of the experiments on laboratory rats.

INFANCY

There is another, more obvious, aspect of the life of a mammal in which skin stimuli are important. This is in the period of dependence at the beginning of post-natal life. A distinctive feature of mammals is the exceedingly intimate relationship which must exist between mother and offspring if the young are to survive. The young come into close contact with the mother during feeding; and as a rule they sleep huddled with the mother, and often with brothers and sisters as well. They are also stimulated by specific kinds of contact. In many, if not most, species, one of the first things a mother does to her newborn young is to lick them all over. To our eyes this suggests cleaning.

But, even if cleaning is one aspect, it is not its only function.

J. A. Reyniers and his colleagues in France recently tried to rear rats without any contact with a mother at all: they delivered the young by Caesarean section and fed them from bottles. The young died. The cause of death was failure to release the urine and faeces. But it was found that, if they were gently stroked, especially in the perineal region, the appropriate reflexes were established and the animals survived. Work in Prague has shown that the same applied to mice. (It does not apply to our own species.)

A very new line of study on infant mammals is that of H. F. Harlow on monkeys (*Macacca mulatta*). This work (already mentioned in *Science News 50*) has shown that for these animals contact with a mother, or mother substitute, is important quite apart from the aspect of suckling or elimination. Profound disturbance of behaviour was observed in infant monkeys if they had no mother to cling to; but it was enough to provide an inanimate model of suitable size, shape, texture, and temperature, to prevent these untoward effects. It would be interesting to know whether the familiar huddling together of small mammals, already mentioned, is of similar importance for them: certainly, it is carried out in situations in which it has no heat-conserving function.

Whatever the significance of huddling, it is evident that cutaneous stimulation is an example of the importance, for the subsequent development of behaviour, of early experience. This is a complicated and important subject in itself. Much of the rigorous experimental work in this field has dealt with the effect of early experience on learning ability or 'intelligence'. Animals that have had a variety of early experience in diverse surroundings are brighter than others that have lived more sheltered lives.

We are less accustomed to thinking of the development of the motivational aspect of behaviour in animals, despite its importance in our own species. But now it seems that experiments on animals are beginning, in this as in other ways, to provide a means of testing hypotheses originating in the study of human behaviour. Let us look again, from this point of view, at the

effect of handling on learning in rats, and in particular at the breakdown of learning if handling is suddenly stopped. Lewis Bernstein, who made these observations, compares this to the breakdown often seen in babies suddenly deprived of their mother's care. Even when the greatest care is taken of the physical condition of the baby there is liable to be a sudden and marked interruption in both intellectual and emotional development. The work of Harlow on infant monkeys seems to fit in with Bernstein's hypothesis. Experimental animals are undoubtedly in a special relationship with the experimenter who handles them. It is therefore possible to suggest that the response of a rat to being stroked by a biologist is to some extent analogous to the response of a child in its so-called object-relationships. Just as these relationships help a child to learn to behave in certain ways so, perhaps, in a similar way, the learning of laboratory animals can be enhanced by contact with an experimenter.

To sum up, it seems likely that the part played by the mammalian skin in behaviour is a bigger one than has been thought. We know that changes in the skin reflect emotional states, as in blushing and paling, and in the rashes that come up when some people are emotionally upset. But it now seems that the skin as a sense organ instigates emotional effects – and incidentally influences intelligence when it does so. There are many questions still to be answered. Are the various forms of cutaneous stimulation that a young mammal has in its nest important for the development of behaviour? Are skin stimuli of major importance in the social relationships of all mammals – including ourselves? Should we cuddle our babies more than we do? None of these questions can yet be adequately answered; they certainly deserve to be investigated.

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THE CHEMISTRY AND
STRUCTURE OF JUTE

W. A. BELL

PROBABLY the most important advance in the textile field in recent years has been the development of new synthetic fibres such as nylon, Terylene, Orlon, Acrilan, etc. In spite of wide general and scientific interest in these new polymeric materials, however, they still constitute only a very small percentage of the total usage of fibrous materials throughout the world. A useful indication of the relative position occupied by the main natural and man-made fibres in general use is given in Table I, which shows world production figures for 1957.

TABLE I
World Production of Fibres, 1957

Fibre	million lb.
Cotton	18,000
Rayon	5,400
Jute	4,000
Flax	3 100
Hemp	2,500
Wool	2,900
Synthetic fibres (nylon, Terylene, Acrilan, etc.)	900

The uses of fibres can be divided for convenience into two main categories, (*a*) for the manufacture of clothing and (*b*) in industrial and engineering applications. While it is difficult to obtain reliable estimates of the quantities of fibre used in different ways, it is probable that in the second category more jute is used than any other single fibre. Jute has a great variety of

uses, and apart from the strictly industrial applications such as in sacks, bags, cordage, hessians, tarpaulins, brattice cloth for mines, and cable wrappings, it is also used to make carpet and linoleum backings, and chair linings and webbings.

It can be said that the development of purely synthetic fibres such as nylon and Terylene is based wholly on the results of scientific research. It would be fair also to say, however, that the immense amount of research that has been done on synthetic polymers has received much of its stimulus from fundamental studies on polymeric materials of natural origin. One of the most important naturally occurring polymers, which has been extensively investigated for many years, is cellulose, the principal constituent of all vegetable fibres.

Most vegetable fibres, however, contain polymeric substances other than cellulose, and different fibres differ in many ways in their properties and their range of usefulness. Why, for example, are Manila hemp and sisal considered to be particularly useful fibres for making ropes? What are the properties of flax that make it especially suitable for sails and heavy canvas on the one hand and for the finest linen damask on the other? Why is jute superior to other fibres as the backing fabric for carpets and linoleum? To obtain answers to questions such as these it is necessary to consider not only the manner of growth and external form of the different fibres, but also the chemistry and molecular composition of all their constituents and the way in which the molecules are arranged in the fibre cells. In discussing the chemistry and structure of jute it will be realized that an understanding of the differences and inter-relationships between it and other natural fibres is of considerable value in interpreting and utilizing the knowledge on jute itself.

THE JUTE PLANT – CULTIVATION AND EXTRACTION OF THE FIBRE

Jute fibre is obtained from the bast of two species of the genus *Corchorus*, family Tiliaceae of the order Columniferae. About forty species of the genus are known but only two, *C. capsularis*, yielding 'white', and *C. olitorius*, yielding 'tossa' jute of com-

merce, are cultivated for fibre. Jute is grown principally in North-Eastern India and East Pakistan, about 1·8 million tons of fibre being produced annually in this region. The only other jute growing countries of any importance are Brazil, the Soviet Union, and China, the last named producing about a quarter of a million tons in 1957.

Seeds are sown in April and May, and the stems are usually harvested soon after flowering, the best yield and quality of fibre being obtained when the plants are in small pods. The stems grow to a height of 8 to 12 feet and reach a diameter of about one inch at the base (see Inset 19). Jute fibres develop in the bark of the stem and in cross-section they appear as wedge-shaped groups or bundles intermingled with patches of sclerenchyma fibres and soft tissue. The bulk of the fibre, forming part of the secondary phloem, is produced by the activity of the cambium. The outermost layer of fibres is developed from the proto-phloem and does not normally exceed 10 per cent of the total fibre content.

After cutting, the harvested plants are tied into bundles and steeped in water for retting. During the retting, which takes from 8 to 30 days, depending mainly on the temperature of the water, the fibres in the bark become separated from the woody stalk through softening of pectic material and the action of micro-organisms on the surrounding tissues. The process requires close supervision, and the time is quite critical, since if the retting is insufficient the fibre will not come away easily and will be contaminated with adhering cortical cells, whilst if it proceeds too far the fibre itself is attacked and weakened. After retting the fibre is stripped from the woody core by hand and is washed and dried. Attempts to extract the fibre by chemical processes and by machinery have been tried, but have not been very successful for reasons of economy and fibre quality.

Structure of the Fibres

The strip of fibres taken from a single plant stem is a complete entity in that the fibres take the form of a tubular, meshy network rather like an elongated stocking. An outer and an

inner network can normally be distinguished. The fibre bundles in this network can be traced all the way from the tip to the root end of the stem, with many divisions and reunions between one bundle and another and between one fibre and another. If a single fine fibre is picked out of the network no more than an inch or two can be followed without coming to a point of division or linkage with another fibre. There is a limit, however, to this splitting tendency and what may be described as a discrete jute fibre is an entity having a diameter of about 40 to 70 microns (one micron equals 0·001 mm). For comparison it may be noted that the diameter of cotton fibres are normally in the range 12 to 20 microns, while the average human hair has a thickness of about 80 microns.

When a cross-section of a single jute fibre is examined under the microscope (Inset 22) it is seen to be composed of a bundle of smaller vessels ranging in diameter from about 7 to 20 microns, which are the ultimate fibre cells. In the plant the number of ultimate cells in a bundle may be as high as 50, but in the process of carding the fibres before spinning this number is reduced to something between 8 and 20. The ultimates can be separated by a chemical treatment and they are then seen to be thin, thread-like cells with lengths ranging from 0·7 to 6 mm.

ULTIMATE CELL TIP

Fig. 1. Interleaved arrangement of cells in jute fibre.

The cells are thus on the average about two hundred times longer than they are broad. They have pointed tapering ends and in the fibre they are arranged lengthwise in an interleaved fashion as represented in Fig. 1. The dimensions of jute fibre cells compared with those of some other common fibres are shown in Table II.

TABLE II
Dimensions of Fibre Cells

Fibre	Average Length (mm.)	Average Diameter (microns)
Ramie	154	35
Hemp	23	25
Flax	35	20
Jute	2·3	17
Sisal	2·2	25
Pineapple	4·5	6
Cotton	25	17

The cells are very firmly attached to one another, and it is generally believed that a cementing substance exists between them. Pectin is known to exist in the interstitial layer (or middle lamella) between growing plant cells, this jelly-like substance being very suitable for maintaining growing cells in close proximity to each other while allowing mutual displacements. Adult cells, however, require more rigid bonding and it is often found in such tissues that the middle lamella is converted to a harder cement in the form of calcium pectate. This may be the cementing material of jute cells, but it has not so far been possible to establish with certainty that any true pectates are present in clean fibre. Another possibility is that a part of the hemicellulosic constituent of the fibre existing in the outermost layer of the cell wall acts as the adhesive material.

CHEMISTRY AND MOLECULAR STRUCTURE OF JUTE

Having examined the jute fibre in as much detail as can be revealed by the eye and by the microscope, one must now consider the finer details of its structure, that is to say, its chemical composition and the molecular arrangement in the cell wall.

Jute has three main chemically distinct constituents: (a) cellulose, (b) hemicellulose, and (c) lignin. These are, in fact, the principal components of the cell walls of all vegetable matter.

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Jute has three main chemically distinct constituents: (a) cellulose, (b) hemicellulose, and (c) lignin. These are, in fact, the principal components of the cell walls of all vegetable matter.

In the growing plant, of course, the cells contain protoplasm and the whole of the tissue is permeated with water. The cell walls of the extracted fibre still contain a certain amount of moisture (10–15 per cent), but the central space is void and all that is left of the protoplasm is represented by a small amount of nitrogenous matter (less than 1 per cent) detectable by analysis. The most characteristic property of the three constituents is that they all have very large molecules, which exist in a wide range of sizes. The molecular weights range from about 3,000 for the smallest hemicellulose molecules to a figure in the region of one million for the largest cellulose molecules.

While the constituents were described above as chemically distinct, cellulose is the only one of the three that can be defined as a pure substance of constant chemical composition and can be said to be chemically the same in all kinds of plant material. The term hemicellulose, however, is applied to a variety of polysaccharide substances which resemble cellulose in being formed of long chains of sugar residues, but which differ in being of smaller molecular size, and in being built up of sugars other than glucose. In any one kind of plant cells, such as jute fibre, the hemicellulose is usually of quite constant chemical composition, and although several polysaccharides may be present, one type of molecular structure usually predominates. The hemicellulose in jute is, however, different from that in hemp, and that in flax and in wood fibres is different again, and so on, although most hemicelluloses show many similarities of structure. Lignin differs from the other two constitutents of jute in not being built up from sugar units. It resembles hemicellulose in so far as it varies in composition from one kind of plant material to another, the variation again being in slight differences in the nature of the building units, and probably in the way the units are combined.

Besides these structural variations in hemicellulose and lignin in different plant material the quantities of these components in association with the cellulose also show wide variation, as illustrated in Table III for various vegetable fibres. In addition to the constituents listed some other minor components are present in

TABLE III
Chemical Composition of Vegetable Fibres

Fibre	α-cellulose	hemicellulose	lignin
Cotton	99	1	0
Flax	75	23	2·3
Hemp	83	14	3·0
Jute	64	24	12
Pinewood	50	24	26
Coir	41	19	40

most fibres but these are not included in the total. These normally consist of wax, mineral matter, and nitrogenous compounds, the total of these three in jute generally amounting to about 2 per cent.

It should be mentioned that considerable variations are to be found in published figures for the amounts of the main components in fibrous materials. This is a reflection partly of the considerable difficulties that have been involved in the analysis and identification of plant components, and partly of changing usage in nomenclature. The term cellulose has often been used to represent the whole of the polysaccharide material in the cell wall, but nowadays is only applied to the pure long-chain polyglucoside, which is also known as α-cellulose. The latter term, however, may also still be used in its strictly analytical sense as representing that part of the polysaccharide material which is insoluble in 17 per cent caustic soda solution. The name pectin has often been used to describe material which would now properly be classed as hemicellulose.

The Cellulose of Jute

Pure cellulose can be decomposed in acid solution and the sole product is pure D-glucose, $C_6H_{12}O_6$, the structural formula of which is shown in Fig 2 *a*. The empirical formula of cellulose, $C_6H_{10}O_5$, indicates that it is built up from glucose by the elimination of one molecule of water for each glucose molecule, and the accepted structure of the cellulose molecule is shown dia-
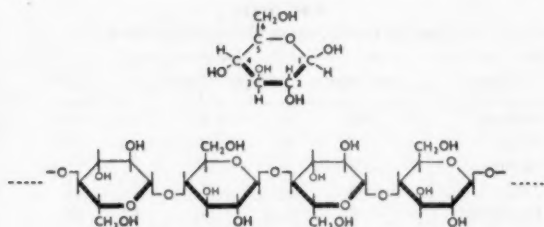
Fig. 2. (*a*) D-glucose. (*b*) Cellulose.

grammatically in Fig. 2 *b*. The anhydro-glucose units are linked into a long chain, the glucose carbon atom number 1 being linked through an oxygen atom to carbon atom number 4 of the next unit. D-glucose can exist in two forms, α- and β-glucose, depending on whether the OH group on carbon atom 1 lies below or above the plane of the ring as depicted in Fig. 2 *a*, and it has been established that in cellulose glucose exists as the β-form.

A number of methods exist for determining the size of large molecules and one of the simplest is to dissolve the polymer in a suitable solvent and measure the viscosity of the solution. Cellulose can be dissolved in cuprammonium hydroxide solution, or it can be nitrated and the cellulose nitrate dissolved in acetone. Viscosity measurements on pure cellulosic material such as cotton fibre, indicate that the average degree of polymerization (number of glucose residues in the molecule) is in the region of 5000. The D.P. is, of course, an average figure and the actual molecular sizes are in fact spread over a considerable range. With lignified fibres such as jute it is difficult to isolate the cellulose without some breakdown of the chains, and there has been some doubt as to whether the D.P. of the cellulose in jute may be considerably lower than that in cotton. Some recent work by T. E. Timmel, however, using a careful nitration procedure, indicates that the average molecular size of cellulose from jute and many other sources does not vary much, as is evident from the figures in Table IV. Results of fractionation studies suggest,

TABLE IV

Degree of Polymerization of Cellulose from Different Sources

Source	Average D.P.
Cotton	4,700
Flax	4,700
Hemp	4,800
Jute	4,700
Ramie	5,800
Wood (various)	5,000–6,000

however, that cellulose from different fibres may differ considerably in the distribution of molecular sizes about the average value.

The Hemicellulose of Jute

The lignin in plant cell walls can be fairly readily, and almost completely, removed by chlorination procedures whereby a soluble chloro-lignin complex is formed. When the remaining polysaccharide material, or holocellulose, is treated with dilute alkali solution the hemicellulose fraction dissolves leaving an insoluble residue of almost pure α-cellulose. In practice, however, the latter invariably contains small amounts of residual non-glucosidic material which is very difficult to remove, and this has given rise to discussion as to the possibility of sugar residues other than glucose being chemically linked in the cellulose structure. No decisive evidence of such linkage has been produced, however. In general, the hemicellulose fraction of plant cells contains a number of different polysaccharides, and several kinds of sugar residues are concerned in their molecular structure, notably xylose, arabinose, galactose, rhamnose, mannose, and glucuronic acid.

When jute holocellulose is treated with 17 per cent caustic soda solution and the filtered solution is acidified and poured into alcohol the major part of the hemicellulose is precipitated as a white flocculent powder. This material appears to have a fairly homogeneous molecular constitution and recent work has estab-
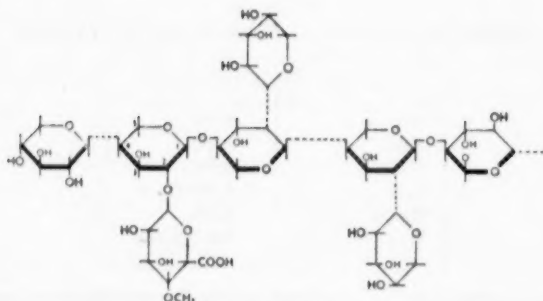
Fig. 3. Jute hemicellulose.

lished that its structure can be represented as in Fig. 3. The molecule, whose average D.P. is about 120, consists essentially of a straight backbone chain of D-xylose residues, with two side-branches also of D-xylose units. Neither the length nor the exact position of the branches is known, however. The molecule also contains a number of short branches consisting of a single residue of 4–O–methyl glucuronic acid, the number of these being one for every seven xylose units. The existence of these carboxylic acid groups in the molecule means that it has a very definite acid character.

It is of interest to note that one of the principal methods used in the elucidation of a structure such as jute hemicellulose is the methylation procedure which was first used more than fifty years ago by Purdie and Irvine. In this method the substance is treated with methyl sulphate so that all the hydroxyl groups are converted to methoxyl groups. The methylated molecule is then hydrolysed with acid to give the individual sugars, which are identified and estimated quantitatively. The identification of un-methylated hydroxyls on the sugars then shows the positions at which the sugar units were joined together, and also where the side chains were attached. The terminal residues of the chains can also be identified and hence the number of main branches established. Today, chromatographic techniques play

an important part in such analyses. In the case of jute hemicellulose the methylation technique established that the D-xylose units in the main chains were linked through carbon atoms 1 and 4 of the xylose, and that the side branches were in all cases attached to carbon atom 2.

The structure just described is that of an isolated fraction of the hemicellulose and there is little doubt that this differs from the material existing in the fibre. Thus, for example, acetyl groups ($CH_3CO—$) are released from jute fibre on treatment with dilute alkali solution and there is good evidence that these are attached to the hemicellulose. They are lost, of course, during isolation of the hemicellulose. The number of acetyl groups corresponds roughly to one acetyl for every two xylose residues, and while their point of attachment is not known, it is possible that they form ester linkages with the hydroxyl groups at positions 2 or 3 of the xylose.

Another difference is that the number of carboxyl groups (—COOH) detectable in raw jute fibre corresponds to only about half the number in the isolated hemicellulose. The hidden carboxyl groups in the fibre make their appearance, however, on treating the fibre with dilute alkali, and it is believed that they may be bonded by ester linkages to the lignin. This is a point of much interest since the possible existence of chemical association between lignin and carbohydrates in plant cell walls has been the subject of considerable speculation.

There are other problems associated with jute hemicellulose that are still unsolved. While the isolated material (containing only xylose and uronic acid residues) forms the major part of the hemicellulose content of the fibre, a number of other sugars has been detected by chromatography in the acid hydrolysate of jute holocellulose, notably galactose, mannose, arabinose, and rhamnose. While caution is needed in accepting that all these sugar residues exist as such in the fibre, since it is known that some sugars can be readily transformed into others under quite mild conditions, the identification of the source of these sugars and the part they play in the hemicellulose structure remains an outstanding problem of jute chemistry.

Lignin

The chemistry of lignin has been studied for more than a hundred years but its molecular structure is still unknown. It is known to be a substance of high molecular weight, built up of small, relatively simple units, but the general overall structure of the molecules remains unsolved. Among the difficulties that have been encountered in studying lignin are, firstly, the fact that it is extremely difficult to separate lignin unchanged from plant material and, secondly, that lignin cannot be hydrolised, nor can it be readily split into simpler fragments without causing drastic changes.

It is probable that only one or two basic units are involved in the structure of lignin derived from many different plant sources. From analytical studies it is evident that the basic building unit is based on the phenyl propane skeleton shown in Fig. 4 *a*. Coniferyl alcohol (Fig. 4 *b*) is found in immature cells of coniferous
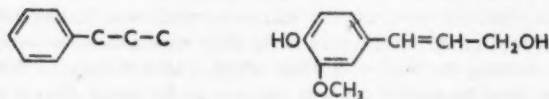

Fig. 4. (*a*) Phenyl propane skeleton of lignin building units. (*b*) Coniferyl alcohol.

wood (as well as sinapinic alcohol in deciduous wood) in which lignification is proceeding, and it is probable that these are the precursors of the lignin molecules. A distinctive property of these simple molecules is the very large number of ways in which they can become linked together in the presence of enzymes found in wood sap, and this undoubtedly accounts for the very many forms in which the phenyl propane unit is found in studies of lignin breakdown products, as well as explaining the overall complexity of the lignin structure.

Most lignin studies have been devoted to wood lignin and very little is known about the lignin of bast fibres or of jute in particular. It is unlikely, however, that appreciable differences

exist. Some recent work has indicated that the presence of lignin in cellulosic material may increase the susceptibility of the cellulose to degradation in the presence of sunlight. It is also probable that colour changes in jute on exposure to light are associated with the lignin and, from the practical point of view, further study of this type of reactivity is likely to be of considerable usefulness.

THE MOLECULAR ARCHITECTURE OF JUTE CELLS

One of the distinctive properties of cellulosic fibres is their high tensile strength (i.e., the load required per unit area of cross-section to break the fibre). This is in the region of 50 to 100 kg/mm² and is similar to that of steel wire. It is generally recognized that this high strength derives from three factors, (a) the chain molecular structure of cellulose, (b) the fact that in general the long molecules tend to lie in a direction parallel to the long axis of the fibres, and (c) the existence of considerable forces of adhesion between adjacent parallel molecules.

Crystallinity

Present-day conceptions of the fine structure of fibre cells are derived very largely from studies by X-ray crystallographic methods and from electron microscope observations. The possibility of using X-ray methods arises from the fact that, in parts of the cell wall, adjacent cellulose molecules assume a highly ordered parallel arrangement, and, in fact, become a crystalline region. Such a crystalline region is short compared with the length of the cellulose molecules and includes only a limited number of chains in the transverse direction. Between the crystalline zones the cellulose chains lose their perfect parallel arrangement and form an amorphous region, but the transition from one region to another is not a sharp one. The overall picture is thus one of crystalline particles embedded in an amorphous matrix, and the diagram in Fig. 5 attempts to give a rough picture of this structure. The crystallites are about 300 Å long and about 50 Å in width (1 Å = 10⁻⁸ cm), but it is probable that the size of the particles varies somewhat in cellulose from dif-
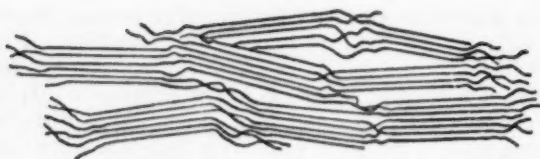
Fig. 5. Crystalline and amorphous regions in cellulose. Each line
represents a cellulose molecule.

ferent sources. Water can penetrate readily into the amorphous
regions of cellulose but cannot enter the crystalline zones where
the lateral bonding of the molecules is much greater.

Another feature of cell wall structure which is below the
limits of observation by the optical microscope has been re-
vealed by the electron microscope. This instrument has demon-
strated the existence of extremely fine threads or fibrils which
have considerable length and vary from 100 to 300 Å wide. In
jute rather flat, ribbon-like fibrils have been observed with a
width of 100 Å and a thickness of about 30 Å. These fibrils are
evidently not very much thicker than the width of the crystalline
regions.

Spiral Structure

It has been mentioned that the cellulose molecules lie roughly
parallel to the axis of the fibre cell. In fact, however, it has been
deduced both from X-ray work and from observations with the
polarizing microscope that the molecules take up a spiral orien-
tation. A diagrammatic representation of this spiral arrange-
ment in the cell wall is shown in Fig. 6.

It has been found that the angle of the spiral with respect to
the fibre axis varies considerably from one type of fibre cell to
another, as shown by the selection of figures in Table v. Some
very interesting conclusions have been reached from observa-
tions on wood fibres and on a wide selection of bast and leaf
fibres. Thus, for example, a study of wood cells showed that the
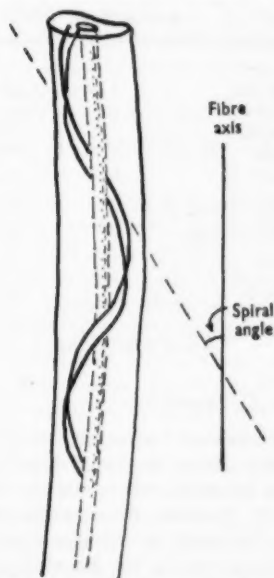longer cells tend to have smaller spiral angles, just as when a

Fig. 6. Representation of spiral orientation of cellulose molecules in fibre cell wall.

spring is elongated the angle of its spiral decreases. Again, observations on many different kinds of leaf fibre cells, covering a wide range of cell sizes, showed that they all have a common feature in that their spirals have the same number of turns per unit length of cell (about 10 per mm), the spiral angle being determined purely by the breadth of the cell. It has also been observed that the amount that a fibre extends before breaking tends to increase with the spiral angle, thus indicating that the extension of a fibre is associated with the straightening of the spirals. A characteristic property of jute fibre is its rather small extension at break, and this is undoubtedly associated with its low spiral angle.

TABLE V
Spiral Angle of Cellulose Chains in Various Fibres

Fibre		Spiral Angle (Degrees)
Bast Fibres	Hemp	6·2
	Flax	6·3
	Jute	8·1
Leaf Fibres	New Zealand Flax	11·1
	Manila Hemp	19·1
	Sisal	23·1
	Coir*	45

* Coconut husk fibre

The Non-Cellulosic Components

In discussing the molecular arrangements in fibre cells, attention has so far been centred on the cellulose, and the question arises as to where the hemicellulose and the lignin are located in the jute cell wall. One thing that must be accepted as established is that they lie outside the cellulose crystallites and form part of the amorphous system. The exact disposition and location of the hemicellulose and lignin are, however, still largely a matter of speculation. It is not known, for example, whether they are intimately mixed with the random portions of the cellulose molecules, or whether perhaps they form some kind of secondary amorphous system in inter-fibrillar spaces.

It has been suggested that some hemicellulose must be quite closely associated with the cellulose, possibly in the fringes of the crystalline zones, because of the extreme experimental difficulty in isolating pure α-cellulose completely free from pentose polysaccharide from jute. The rather ungainly molecular shape of the main hemicellulose fraction, however, does not suggest that it would fit very readily into a region of fairly closely packed cellulose molecules. There is some evidence too, from staining observations, that the lignin may exist in rather higher concentration near the outer boundary of the cell wall. A distribution

of lignin of this kind in wood cells has been very elegantly demonstrated by Lange in Sweden using a micro-spectrographic technique.

SIGNIFICANCE OF SOME FIBRE PROPERTIES

In this brief account of the chemistry and structure of jute fibre, some mention has been made of the differences and relationships that exist between jute and other commercially used vegetable fibres. At the beginning, some questions were posed concerning the special usefulness of different natural fibres for specific purposes, and it is of interest to examine how far such questions can be answered in terms of present knowledge of fibre structure and molecular arrangement. While complete answers cannot be expected, some possible correlations can be discerned. It seems probable, for example, that the usefulness of Manila hemp and sisal for ropes may be associated with the high spiral angle of the cellulose molecules in the cell walls, which would indicate a large capacity to absorb high shock loads. Again, the special ability of ramie and flax fibres to be spun into exceptionally fine yarns of high strength is undoubtedly connected with the high average values of the ultimate cell length of these fibres. Finally, a notable property of jute is the very small extension of the fibres on application of a load, a factor which is associated with its low spiral angle and possibly also with its degree of lignification. This property gives jute a special usefulness in applications requiring high dimensional stability, e.g. as backing for carpets and linoleum.

CONCLUSION

The account just given has indicated some aspects of our present knowledge of the chemical and physical properties and the molecular structure of jute. This knowledge provides an indispensable background for applied research aimed at improving and extending the usefulness of jute as a textile fibre. Some of the practical problems involved include the protection of jute materials against degrading influences such as microbiological rotting, sunlight, weathering, the action of various chemical

substances which come into contact with the fibre during its use, and abrasive conditions. They include also the study of the behaviour of fibres during processing operations such as carding, spinning, and weaving. Progress in these and other aspects of fibre technology relies on the continuous widening of our knowledge of the basic properties of the fibres themselves.

A NEW APPROACH TO
THE TEACHING OF HEAT

G. L. ROGERS

In fifteen to twenty years' time, Australia and New Zealand will be producing large quantities of iron and steel: the countries of South-east Asia will be manufacturing cotton textiles of steadily increasing quality: the primary wool-producing countries will be producing their own woollen fabrics and exporting them in the finished state: coal will no longer be a major British export. As a result we in Britain will be driven to make more and more complicated scientific and technical machinery and equipment, in order to import our food.

While we are busy trying to train a new generation to understand and follow the great technical change-over they have to accomplish, our task is made much harder by the vast increase in technical knowledge itself: we don't really know what to include, what to leave out. Faced with this need for compression, a teacher will often find the answer in making a fresh start. By approaching the subject from a new angle, he may be able to teach more economically and efficiently. This may result from the disappearance of unwanted material, and the derivation of important results from comparatively few, clearly stated, fundamental principles.

The subject of elementary heat lends itself particularly to such a fresh start. When asked to give an elementary heat course in New Zealand a few years ago, the writer decided to try a new approach. For years it has been customary to open text-books of heat and find at the beginning a chapter on temperature. This is, indeed, the historical order in which the science of heat developed, but is it the logical way in which to present it today?

It happens that temperature is one of the most subtle and

difficult concepts in thermodynamics. Many good students have reached a ripe old age without thoroughly understanding it. One can mention shortly such modern usages as 'colour temperature', 'electron temperature', and 'noise temperature'. The confusion in these fields merely illustrates the difficulty of the concept. Some sort of understanding can come from statistical mechanics, but it is really a concept on which much more fundamental thought is still required.

Heat as a form of energy

It was decided to start, instead, in the middle of the nineteenth century. In an age of electric fires and electric kettles it seemed fair to start from the basic assumption that heat is a form of energy. It is appreciated that this came rather late in the history of the subject, but it was known to scientists a century ago, and may be presumed to have penetrated to the general public by now.

Comparison is made between heat as a form of energy and other forms of energy, particularly water power and electricity. This was easy in New Zealand because most of the electricity comes from water power, and a fall of 20 feet in the level of Lake Taupo spreads panic through the North Island. But the whole idea of potential energy is familiar enough anywhere: the energy possessed by a mass by reason of its height above an arbitrary zero – floor level or sea level for example. Similarly, the energy in an electrical condenser can be represented in terms of the charge and the voltage.

It is readily pointed out that all these forms of energy can conveniently be measured by multiplying together two factors. One is proportional to the quantity of matter or electricity involved: the other is not. In the language of thermodynamics, one is an 'extensive' quantity and the other is an 'intensive' quantity. It was found, rather surprisingly, that the use of these terms 'extensive' and 'intensive' is far better understood by elementary students than was expected. If, then, heat is a form of energy, it must be capable of measurement by multiplying an 'extensive' and an 'intensive' term.

Temperature as a potential

The heat stored in a mass of hot water is clearly proportional to the mass of water involved. That is the 'extensive' factor. But it also depends on the 'hotness' of the water. That is the 'intensive' factor because it is independent of the quantity of water. This 'intensive' factor we call temperature. Temperature may, therefore, be measured in principle by determining the amount of energy a hot body gives out in cooling to room temperature – or to any arbitrary zero such as the ice-point. It will be seen that temperature is now a type of potential, analogous to voltage, or height above sea level. Indeed there are very real advantages to be gained by likening room temperature to sea level as a convenient zero from which the potential may be measured. In many problems with heat engines the analogy is particularly fruitful.

It is a passing irony of history that the term 'thermodynamic potentials' should have been early applied to four other functions, and this has undoubtedly impeded the recognition that temperature also has important properties of a potential.

The Measurement of Temperature

The measurement of temperature in terms of the energy given out by a hot body (say 1 gram of water) in falling to the ice-point is not in fact practicable (except possibly in a Bunsen ice calorimeter), so we do what the water engineer often does in measuring the 'head' of water on his turbines. Instead of dropping a surveyor's measure over the dam wall, he normally measures the head by a Bourdon gauge. That is, he measures it in terms of the behaviour of an arbitrarily fabricated flat coil, which unwinds to different extents under different heads, i.e., he uses a purely empirical instrument which has to be calibrated in some way. Similarly, the heat engineer can use an empirical instrument to measure temperature.

The practical scales used in temperament measurement are, of course, linked with history. It is as though two large and steady lakes were available at different heights, and all heads could be

calibrated in terms of the height between them. If it is agreed, as a matter of practical politics, that you want a zero and a definite size for your unit, the ice point and the steam point give you the necessary basis. And for many purposes one device is as good for subdividing them as another. Thus, the basic concept of temperature as a form of potential, and of a hot body as having potential energy, is first established, and practical thermometry is developed afterwards as a method of measuring it.

Electrical Measurement in Heat

At this point two courses are open to the teacher. The more conservative may go on from thermometry (regarded as an attempt to express a basic factor) to calorimetry, the method of mixtures, and the rest. For these, we have merely written a new prologue. But for the more adventurous there are new fields to be explored. Few people with any sense of precision measurements can regard the method of mixtures as anything better than amateur dabbling. A study of original papers shows that all serious experiments on heat nowadays are based on the electrical measurement of a given quantity of energy which is supplied to the system with precisely measurable results – a given rise of temperature, or the evaporation of a given mass of liquid, for example. Indeed, during the 1930s the custom of using electrical units and then converting them to all sorts of different types of calories was causing embarrassment and misunderstanding. So it was wisely decided to leave all such measurements in poules, and the 7th edition of the well-known *Kaye and Laby* tables of physical constants has all such results given in work units.

This means that the student is faced at once with the Nernst calorimeter and the Henning method for latent heat (which can be done very easily and very accurately in the laboratory). He then meets Searle's bar (electrical heating) for thermal conductivity, and discovers that all the experiments from Joule to Osborne, Stimson, and Ginnings were really designed to measure the specific heat of water in work units. The fact that they all give essentially the same numerical value is proof of the basic

assumption that heat is a form of energy. The specific heat of water in joules would not be constant if it were not. Thermal expansion and hygrometry may be inserted where appropriate, and, of course, the gas laws form the stepping-stone to a more fundamental view of the whole subject with the introduction of the idea of an absolute zero, and the development of thermodynamics as we have it today.

PRACTICAL EXPERIMENTS

This new approach to the treatment of heat requires a thorough revision of the associated practical experiments. Some, of course, remain: the gas thermometer, Boyle's Law, thermal expansion, hygrometry, vapour pressure, Clement and Desormes and any others that do not involve measuring energy in calories. Thus all the 'method of mixtures' experiments are omitted, and we need particularly some experiments to measure specific heat, latent heat, and thermal conductivity directly in work units or joules. Fortunately, it is not particularly difficult to provide suitable experiments on all these measurements which can give a student some idea of the attainable accuracy of electro-thermal measurements.

Specific Heat

Considering that it was first published a quarter of a century ago, Ferguson's method for the specific heat of a liquid is strangely neglected in the teaching of heat. In the research laboratory, with platinum resistance thermometers, an accuracy approaching 1 in 1000 is claimed. A student using a mercury thermometer should get somewhere around 3 per cent. It is basically similar to the old experiment on the specific heat of a liquid by cooling, but the comparison run with water is eliminated, and an electrical measurement takes its place.

The apparatus consists essentially of a calorimeter with the liquid, a heating coil, and some type of screened surroundings, which remain at essentially the same temperature throughout the experiment. The experiment is done in two parts: first the

liquid is heated to a suitable temperature, embracing, if possible, the range over which the specific heat is desired, and an ordinary cooling curve (temperature against time) is plotted. This should be done as accurately as possible, because it is the heart of the experiment, and a thermometer calibrated to 0·2° C is very desirable. At any given temperature, the system (liquid, calorimeter, thermometer, etc.) is losing energy to the surroundings at a definite rate, which depends, for given conditions of surfaces, air, etc., only on the two temperatures involved. The rate of loss of energy equals mass multiplied by specific heat multiplied by rate of fall of temperature. It is measured in the same units as the specific heat, and if the specific heat is in joules per gram per °C, the rate of loss of energy is in joules per sec, or in watts.

Now this rate of loss of energy, for given conditions, is easily found by determining the electric power necessary to replace it exactly and keep the system at a definite temperature above the surroundings. For teaching purposes, it is not very important to specify the excess temperature beforehand. The student is therefore told to apply a given power to the system, and find the equilibrium temperature to which it tends. Thus if 2·5 watts keeps 100 grams of liquid at 32·6° C when the surroundings are at 18° C, then the system is clearly losing 2·5 watts to its surroundings. Reference is now made to the cooling curve. A tangent is drawn to the curve at 32·6° C (e.g., by reflecting it in a mirror, which becomes a normal to the curve at this point), and the rate of fall of temperature determined. If this is 0·6° C per minute, or 0·01° C per second, the specific heat is:

$$\text{Specific heat} = \frac{\text{Rate of loss of energy}}{\text{mass} \times \text{rate of fall of temp.}} = \frac{2·5}{100 \times 0·01}$$

$$= 2·5 \text{ joules per gram per } ° C$$

This value is quite reasonable for a number of readily obtainable oils, which can be used safely from 40° C down to room temperature. A small correction should be made for the thermal capacity of the calorimeter and thermometer, but this is readily done.

Latent Heat

Another simple experiment can be done to determine the latent heat of evaporation, by a modification of Henning's method. A simple arrangement, suitable for a school laboratory, is shown in Figure 1. An ordinary thermos flask is used to minimize heat losses, and the electrical energy is conveniently supplied by a 250 watt immersion heater of the type used to heat a cup of water. Normally, a control resistance is included in series, and the power is monitored with an A.C. voltmeter and ammeter of high quality. A current of about 1·5 amps at about 160 volts has been found to be quite satisfactory.

The apparatus is filled with distilled water (this increases the life of the element) and is allowed to boil steadily – the water condensing being run to waste. A weighed beaker is then placed under the outflow for 15-20 minutes, and the amount that collects is determined by reweighing. The flow of cooling water should be fast, and the condensed water should be cool by the time it reaches the beaker. The time of collection should be determined to the nearest second, and the power input should be monitored during the run. The latent heat is then given by

$$\text{Latent heat} = \frac{\text{Average power input} \times \text{length of run in seconds}}{\text{weight collected}}$$

With suitable lagging the heat losses are very small, and students consistently get values in the range of 2240–2280 joules/gram for the latent heat of water at 100° C. This type of experiment compares favourably in accuracy with the 'method of mixtures' experiment where dry steam is blown into water.

If desired, heat losses can be eliminated by repeating the experiment at a lower power level, say 1 amp. The rate of heat loss depends mainly on thermal conduction between a body at 100° C and one at room temperature, and is independent of the rate of supply of electrical energy. A check of this type has been applied, which suggests that the rate of heat loss is so small as to be practically negligible.

The latent heat of fusion can be determined by the usual

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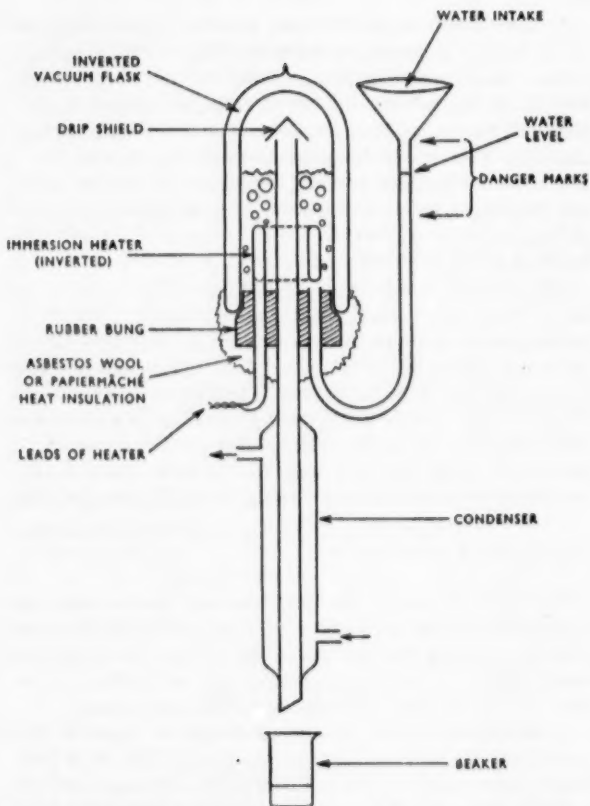The latent heat of fusion can be determined by the usual

Fig. 1. Apparatus for the determination of the latent heat of evaporation.

method of cooling, with a modification equivalent to Ferguson's method. In this case, however, the adjustment is a little more difficult, as the electrical power has to be arranged to hold the liquid at some point 1 to 3° C *above* the melting point to make sure it all remains liquid. A correction, by Newton's Law, is then necessary to get the power radiated at the melting point. This power multiplied by the time of solidification divided by the mass of material gives the latent heat of fusion.

Other Heat Experiments

Any of the standard methods for the mechanical equivalent of heat can be adapted to measure the specific heat of water in work units, or indeed of any other liquid. The change is one of interpretation rather than experimental details, though any corrections for the water equivalent of the calorimeter must be made in work units – fortunately, specific heats are now available in *Kaye and Laby* in work units, and many of these have been directly determined in work units by electrical methods.

Thermal conductivity may be determined by Searle's bar using an electrical heater. The energy supplied here is assumed to arrive at the far end. (This can be checked independently by measuring the rise in temperature of the cooling water, and is found to be a fair assumption.) The thermal conductivity is then expressed in joules per square centimetre per unit temperature gradient.

Copper is a good conductor and its specific heat is readily obtained in work units by winding a coil on a copper plug screwed into a block, and determining the electrical energy needed to heat it a few degrees Centigrade. A similar apparatus, heated at one end, can be used to determine the thermal conductivity of a thin slab of poor conductor placed between two copper blocks. Both devices have to be well lagged.

It might even be worth considering Bunsen's ice calorimeter as a student experiment. This requires a little care in setting up, and should always be surrounded by a bath at 0° C. It is readily calibrated directly in joules. A small heating coil is inserted in the thimble and allowed to reach 0° C. A small known amount

C

of electrical energy is then liberated in a comparatively short time, and the change of mercury position noted. It can then be used to determine heats of reaction, or any of the more normal quantities, directly in joules.

The above outline course in experimental heat has not been developed in its entirety; in particular the Ferguson methods have not been attempted as elementary experiments, nor has the Bunsen ice calorimeter been tried. But all the other experiments have been tried and are reasonably satisfactory. It would seem, therefore, there is no basic reason why a full theoretical and practical course of heat in work units should not be given to the student.

FURTHER READING

Roberts, J. K.: *Heat and Thermodynamics*, 4th edition, revision by A. R. Miller (London, Blackie, 1951), contains articles on Nernst calorimeter; Henning's method; Ferguson's method; thermal conductivity of poor conductors; Bunsen ice calorimeter; etc.

MICROBES IN INDUSTRY

A. H. ROSE

THROUGHOUT the centuries, Man has been very active in cultivating plants and domesticating animals, but it is only during the last few decades that he has begun to appreciate the advantages that can be gained from harnessing the activities of micro-organisms. Yet we know that many early civilizations knew how to use yeasts for baking and brewing; and the retting of flax, the process in which the pectic substances surrounding the fibres in the flax stem are digested by micro-organisms, is probably as old as baking and brewing. But the microbial world had yet to be discovered when Man developed these processes, so that, at the time, he was more inclined to attribute the changes brought about to supernatural forces than to living organisms.

In fact, it was not until 1676 that the Dutchman Antonie van Leeuwenhoek became the first man to make a lens powerful enough to observe the cells of micro-organisms. And for over a century after this, microbiologists were preoccupied with describing and classifying the newly discovered microbial world. But then came what has been aptly described as the Golden Age of Microbiology, because during the nineteenth century a series of discoveries was made that had a profound effect on future developments. Some of the most far-reaching of these were made by the Frenchman Louis Pasteur who, over a period of about thirty years, studied most of the traditional fermentation industries, including brewing, wine-making, and vinegar production. His major discoveries are embodied in the monumental *Études sur la bière*, published in 1876, in which he first put forward the idea that different types of fermentation – alcoholic, lactic, acetic, etc. – were caused by specific micro-organisms. Another outstanding discovery of this era came from

the German Robert Koch, who developed techniques for isolating microbes in pure culture, that is in cultures consisting of only one strain or species of micro-organism. This development was of considerable importance in the fermentation industries. Previously, fermentations had been carried out using mixtures of microbes, but, as a result of Koch's discovery, it became possible to select the principal micro-organism in the mixture – the star performer – and use this in pure culture. Not long afterwards, the Danish botanist, Emil Christian Hansen, introduced pure cultures of yeasts into the brewery.

The closing years of the nineteenth century also witnessed the birth of biochemistry. When, in 1897, the Buchner brothers demonstrated alcoholic fermentation in cell-free extracts of yeast, they not only exploded once and for all the 'vitalistic' theory of fermentation, but also sparked off a whole series of studies that ultimately led to a complete elucidation of the dozen or so enzyme reactions involved in alcoholic fermentation. Studies into the biochemical activities of other micro-organisms soon followed, and in fact this led to the first major advance in modern industrial microbiology. During the First World War, there developed in Britain an acute shortage of acetone, which at the time was being used in munitions factories for dissolving cordite. This threatened to jeopardize the war effort, so much so that an intensive search was made for alternative sources of the solvent. For some time, Chaïm Weizmann had been studying the chemical activities of the bacterium *Clostridium acetobutylicum*, with the idea of using the butanol produced by this organism in the manufacture of synthetic rubber. But it was the acetone that is produced along with butanol that first led to its being used in an industrial process. The acetone-butanol fermentation differed in many ways from the familiar alcoholic fermentation by yeast; for example, the bacterium was a much more difficult micro-organism to propagate, and yields were only about one-tenth of those obtained during alcoholic fermentation. Nevertheless, Britain had good reason to be thankful for Weizmann's pioneer work, and when later he became the first President of the new State of Israel, he
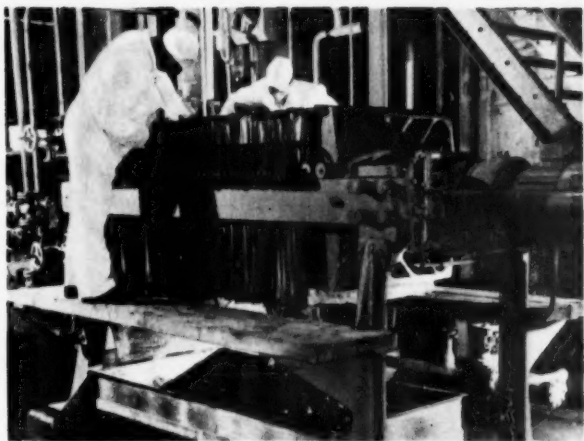
1. Ten-thousand-gallon fermentation tanks used in the production of penicillin and streptomycin. (*Courtesy of Glaxo Laboratories Ltd.*)
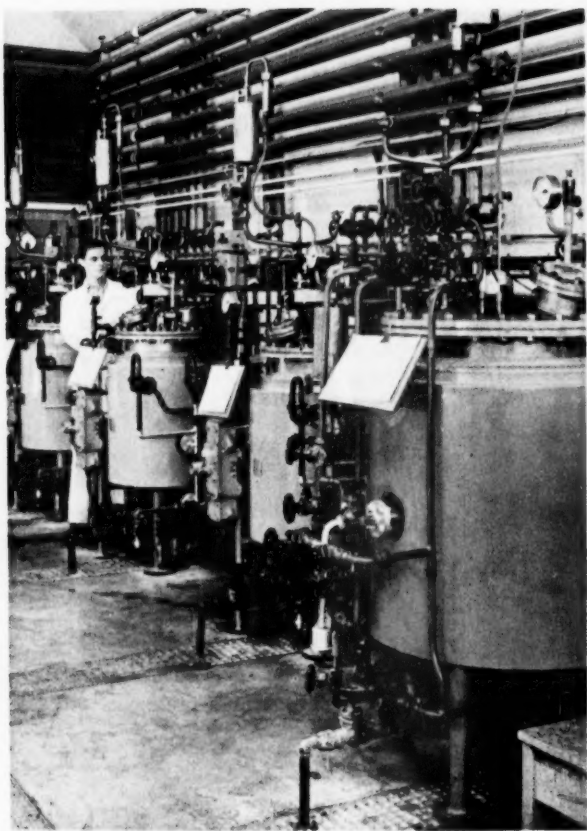
2. Small scale experimental fermentation tanks for the production of antibiotics. (*Courtesy of Beecham Research Laboratories Ltd.*)

3. Large filter press used for separating crude terramycin during extraction of the antibiotic from the culture medium. (*Courtesy of Pfizer Ltd.*)
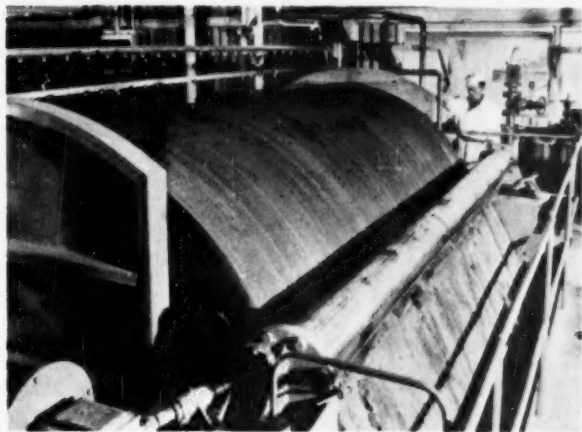

4. Rotary filter for separating solid material from microbial cultures prior to extraction of the fermentation product from the culture medium. (*Courtesy of Pfizer Ltd.*)

5. Photomicrographs of moulds used in industrial processes. (a) A species of *Penicillium* ($\times 550$) used in the manufacture of penicillin. (b) *Rhizopus* mould ($\times 370$), species of which are useful in carrying out steroid transformations. (c) *Aspergillus terreus* ($\times 370$) employed in the industrial production of itaconic acid, an organic acid that finds applications in the resin and detergent industries. (*Courtesy of Beecham Research Laboratories Ltd.*)
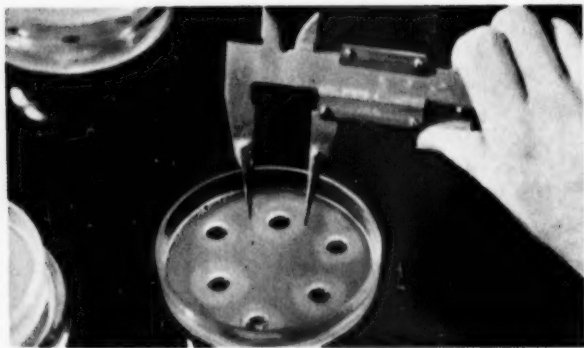
6. Measuring the potency of antibiotics by plate assay. Solutions of antibiotic are placed in holes in a solid agar medium seeded with a suitable test micro-organism. When the plates are incubated, the test micro-organism grows to give the agar a cloudy appearance. But around the holes, zones of inhibition appear, where growth of the micro-organism has been prevented by the antibiotic diffusing out from the hole. (*Courtesy of Beecham Research Laboratories Ltd.*)
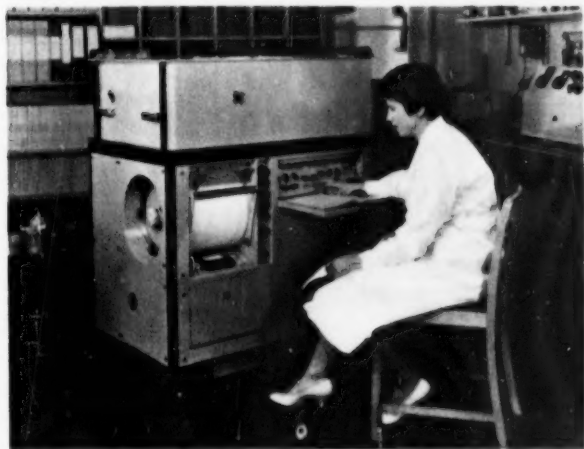
INFRA-RED SPECTROSCOPY
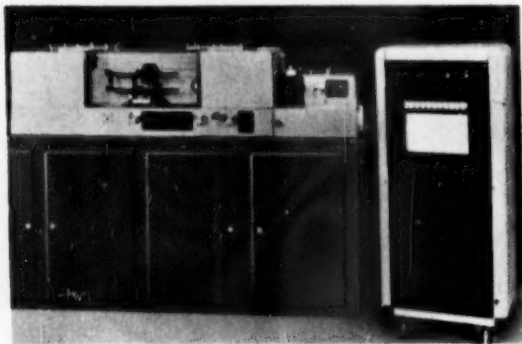
7. Hilger H800 infra-red spectrophotometer with, on right, the recorder and amplifier. (*Courtesy of Hilger and Watts Ltd.*)

8. Grubb Parsons double-beam grating infra-red spectrophotometer. (*Courtesy of Sir Howard Grubb, Parsons and Co. Ltd.*)

9. Unicam SP100 infra-red spectrophotometer. (*Courtesy of Unicam Instruments Ltd.*)

10 *a*, *b*, and *c*. Chicago 1949–1955–1959. Slum clearance and renewal of a central ward. At the bottom right can be seen a section of the overhead railways of the Illinois Central which serves the suburbs, Indiana towns, and New York. Just out of the picture is the artificial foreshore of Lake Michigan, the town's most important amenity. The town is in grid-iron layout. The rectangular or quadratic blocks indicate the harshly planned thinking of this flat town and its developers. Its deterioration seems much more rapid than that of any European town, and its rebuilding involves vast replanning projects. The old congested parts are seen as well as the clearings with high apartment buildings, lawns, and greater breathing space. (*Courtesy of Chicago Aerial Industries Inc.*)

11 *a*, *b*, and *c*. Franklin Park 1949–1955–1959. Urban growth to the west of Chicago. The photograph shows suburban housing, and commercial activity on Grand Avenue. Farms are gradually being invaded as Chicago grows and grows. The older development was rectangular like the rest of Chicago, but, instead of apartment houses, here we have single family dwellings. The postwar trend has been towards curvilinear streets with cul-de-sacs, which give groups of families a community feeling and privacy from through traffic. It might be thought that this gives a country lane type of development, but the symmetrical layout shows that rectangularity is still part of the urban life of the United States. In fact, the next step is back to a grid-iron layout which is more economical. Land values and building costs have gone up so the lots are smaller and the driveways shorter. Fewer trees and greater densities show that this area in this quickly changing town may have passed its peak. Newer upper class suburbs are being founded elsewhere. (*Courtesy of Chicago Aerial Industries Inc.*)
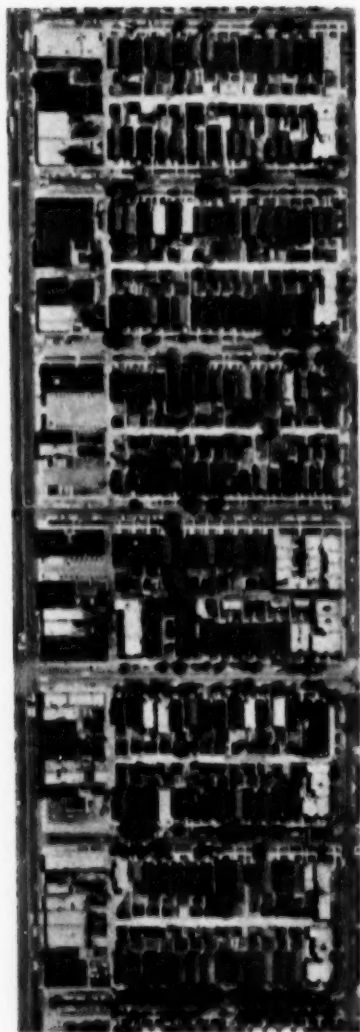
12. West Side Chicago 1958. An example of a built-up area, stationary and lower middle class. The six blocks are between 63rd and 64th Street with their bus routes. There are apartment buildings on the corners and back-to-back buildings with drive lanes in the middle. People drive their cars into the garages and enter their homes from the back; two families live on each floor with the entrance in the middle. From the shadows we know that the buildings are three to five storeys high. They are brick built and lined with white cement, a style current in the 1920s. The inhabitants probably spend long hours at work and there is little scope for outdoor activities in this area – no playing fields, no schools, no churches, but several filling stations with islands for the pumps can be seen. There are few trees, no gardens, indeed no vacant lots, but the area, while shoddy, is still good and old enough to accommodate at least second generation Americans. (*Courtesy of Chicago Aerial Industries Inc.*)

13. Jute is the bast of two species of *Corchorus* grown principally in North-Eastern India and East Pakistan. Stems reach a height of 8 to 12 feet and are harvested soon after flowering.

14. Cutting jute stems in East Pakistan.

15. Retting to extract the jute fibre from the reeds.

16. Cross-section of single jute fibre showing that it is made up of a bundle of smaller vessels of diameter 7 to 20 microns. These are the ultimate fibre cells.

made sure that a department of industrial microbiology was instituted in the university there.

Meanwhile, considerable interest had been aroused following the production on an industrial scale, by micro-organisms, of citric acid, a substance that is widely used in the food industries for imparting an acid flavour to foodstuffs. The microbial production of citric acid was of particular significance in that it employed a mould, one of a group of micro-organisms that had hitherto been somewhat neglected as being normally associated with decay and spoilage. Moulds are notoriously variable in their chemical activities, a fact that was known to Albrech von Haller when, over 200 years ago, he described them as a 'mutable and treacherous tribe'. Not unexpectedly, therefore, the citric acid fermentation took time to perfect; however, the problems were finally surmounted, and the production of citric acid by strains of *Aspergillus niger* is still today a flourishing industrial process.

The success of these pioneer industrial fermentations, coupled with an increasing awareness of the chemical potentialities of micro-organisms, led to the development of several further processes. Other organic acids, including lactic and gluconic acids, were soon being manufactured on an industrial scale using moulds. Ethanol, a valuable industrial solvent, was obtained by distillation of a molasses medium that had been fermented with yeast. And by including sulphites in the yeast medium, it was discovered that considerable quantities of glycerol could be produced at the expense of ethanol: this too was developed on an industrial scale, although the process has apparently been abandoned now that glycerol can be obtained much more cheaply from the fat industry. A shortage of natural rubber during the Second World War again led to a search for synthetic substitutes, and production by the bacteria *Bacillus polymyxa* and *Aerobacter aerogenes* of 2,3-butanediol, a raw material that can be used to make synthetic rubber, was very closely examined. A microbial product of a rather different type that has proved immensely valuable is the plasma substitute dextran, which is a high molecular weight polysaccharide produced from cane

sugar by the bacteria *Leuconostoc dextranicum* and *L. mesen-teroides.* But undoubtedly the most spectacular contribution that industrial microbiology has yet made to the economy of man-kind has been the manufacture of antibiotics. The immense value of these microbial products in combating a wide variety of human, animal, and plant diseases is well known, and in recent years they had found additional uses as supplements in animal fodder.

However, the flush of success that followed the discovery of antibiotics was tempered somewhat by the growing realization that the industrial chemist was now able to manufacture quite cheaply several products that had hitherto been mainstays of the fermentation industries. Industrial alcohol, for example, can now be produced synthetically from ethylene that is formed during the cracking of petroleum, as also can butanol; and in each case, the synthetic product is cheaper than that made by fermentation. To meet this challenge, the industrial micro-biologist has become more versatile and far more subtle, and during the last few years this has led to considerable changes in the scope of microbiological industry. The continuing success of the antibiotics industries showed quite clearly that production of complex organic substances by micro-organisms was less likely to meet severe competition from the industrial chemist, and so considerable efforts are being made to exploit to the full the synthetic capabilities of micro-organisms. As a result, pro-gress in industrial microbiology is now more than ever depen-dent upon a thorough understanding of the chemical activities of micro-organisms, so that before considering some of the more recent advances, we should first take a closer look at the behaviour of the organisms employed.

CHEMICAL ACTIVITIES OF MICRO-ORGANISMS

The microbiologist is concerned with the study of those living organisms that can be seen only with the aid of the microscope. With the exception of the protozoa, these are all microscopic plants; they include algae, bacteria (among which are classified the actinomycetes) and fungi (in which are grouped the moulds

and yeasts). Microbes are simple organisms, and many of them, notably the yeasts and bacteria, consist of single discrete cells, each cell having an independent existence. Others, such as the actinomycetes and moulds, show a slightly greater degree of organization in that the individual cells are often attached end to end to form a strand or mycelium.

Now the surface area to volume ratio for a microbial cell is enormously greater than for any other type of living organism. A bacterial cell, for example, measuring 0·5 microns in diameter, has a ratio of around 120,000, whereas comparable figures for a hen's egg and for a 12-stone man are approximately 1·5 and 0·3 respectively. Since, in general, the chemical activities of a living organism increase with the surface area to volume ratio, it follows that, weight for weight, micro-organisms are far more active metabolically than are more highly organized plants and animals. Thus, a bacterial cell may ferment 1000 times its own weight of lactose in an hour, but for a man to metabolize a comparable quantity of sugar would take half a lifetime! It is this high degree of chemical efficiency that makes micro-organisms such valuable agents in industrial processes.

Chemical analyses show that the substance of microbial cells, like that of all living cells, is made up of complex organic molecules, including carbohydrates, lipids, proteins, vitamins, and nucleic acids. Protein accounts for almost half the dry weight of many microbial cells. A growing cell must therefore have available a suitable source of food for use in manufacturing new protoplasmic material. Some microbes are able to build up or synthesize new cell material starting with such simple compounds as water, and carbon dioxide and nitrogen gases; these are termed autotrophs. In these micro-organisms, the energy that is required to drive the synthetic reactions is obtained either from the sun, as in those microbes (such as the algae and the photosynthetic bacteria) that possess the green photosynthetic pigment chlorophyll, or from simple chemical exothermic reactions. The other major group of micro-organisms are the heterotrophs. These do not possess such extensive synthetic abilities as the autotrophs, and therefore need to be supplied

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and yeasts). Microbes are simple organisms, and many of them, notably the yeasts and bacteria, consist of single discrete cells, each cell having an independent existence. Others, such as the actinomycetes and moulds, show a slightly greater degree of organization in that the individual cells are often attached end to end to form a strand or mycelium.

Now the surface area to volume ratio for a microbial cell is enormously greater than for any other type of living organism. A bacterial cell, for example, measuring 0·5 microns in diameter, has a ratio of around 120,000, whereas comparable figures for a hen's egg and for a 12-stone man are approximately 1·5 and 0·3 respectively. Since, in general, the chemical activities of a living organism increase with the surface area to volume ratio, it follows that, weight for weight, micro-organisms are far more active metabolically than are more highly organized plants and animals. Thus, a bacterial cell may ferment 1000 times its own weight of lactose in an hour, but for a man to metabolize a comparable quantity of sugar would take half a lifetime! It is this high degree of chemical efficiency that makes micro-organisms such valuable agents in industrial processes.

Chemical analyses show that the substance of microbial cells, like that of all living cells, is made up of complex organic molecules, including carbohydrates, lipids, proteins, vitamins, and nucleic acids. Protein accounts for almost half the dry weight of many microbial cells. A growing cell must therefore have available a suitable source of food for use in manufacturing new protoplasmic material. Some microbes are able to build up or synthesize new cell material starting with such simple compounds as water, and carbon dioxide and nitrogen gases; these are termed autotrophs. In these micro-organisms, the energy that is required to drive the synthetic reactions is obtained either from the sun, as in those microbes (such as the algae and the photosynthetic bacteria) that possess the green photosynthetic pigment chlorophyll, or from simple chemical exothermic reactions. The other major group of micro-organisms are the heterotrophs. These do not possess such extensive synthetic abilities as the autotrophs, and therefore need to be supplied

with more complex organic substances as raw materials in their synthetic reactions. A supply of energy is obtained by breaking down various energy-rich organic substances, notably sugars. Heterotrophic microbes vary considerably with regard to the substances or nutrients they can use as a source of food. Moulds and actinomycetes usually grow quite well in simple sugar-salts media, but some yeasts and bacteria are more selective, and will grow only in the presence of rich organic compounds. A knowledge of the nutritional requirements of a microbe is essential to the industrial microbiologist who must provide a cheap source of food for it in order to make an industrial process economically feasible. In most large-scale processes, comparatively inexpensive raw materials, such as cane- and beet-sugar molasses, and various industrial wastes, are used. Moreover, microorganisms vary in their requirements for oxygen, temperature, and acidity, and these too need to be adjusted to suit the needs of the organism being cultivated.

Inside the cell, nutrients undergo a series of chemical modifications, as a result of which they either decrease (dissimilation) or increase (assimilation) in molecular complexity. The metabolic reactions concerned in these chemical transformations are catalysed by enzymes that are produced by the cell. Enzymes are proteins, but frequently they require a non-proteinaceous prosthetic group, or co-enzyme, for their activity: several of the B-group vitamins act as co-enzymes in this way. Although most of the enzymic reactions take place inside the cell, a nutrient is sometimes attacked before it enters the cell. Thus some microbes secrete hydrolytic enzymes that break down complex molecules such as polysaccharides and proteins to give smaller molecules that can more readily enter the cell. Also it is important to note that the enzymic equipment of a microbial cell is not static, but that it can to some extent be altered and modified to suit the type of molecule being metabolized. For example, by successively culturing a microbe in the presence of increasing concentrations of a substance that it initially cannot metabolize, the organism can frequently be induced to synthesize an enzyme system that enables it to attack that nutrient. Another way of

modifying the enzymic capacity of a micro-organism is to isolate mutant strains of the organism by any of the usual methods, such as ultra-violet irradiation or treatment with muta-genic chemicals. Both methods have been used successfully to alter the enzymic equipment of micro-organisms for use in industrial processes.

The industrial microbiologist is concerned primarily with the end products of microbial metabolism, be it new cell material, or various substances that are excreted by the micro-organism, including metabolic waste products, such as ethanol, that are left after the microbe has broken down sugars to provide energy. However, an understanding of the intermediate metabolic re-actions that occur inside the cell is proving of considerable value, because, armed with this knowledge, the microbiologist can often improve the yield of a desired end product by feeding to the growing microbe an intermediate in the biosynthetic chain. This has been used with great success in the manufacture of penicillin. Alternatively, a chain of metabolic reactions can often be diverted artificially, to produce some entirely different major product. An example of this has already been noted in the manufacture of glycerol by *Saccharomyces cerevisiae* in media containing sulphites. The synthetic chemist too can often profit by studying the ways in which a micro-organism carries out a particular synthesis.

THE ANTIBIOTICS ERA

Today, antibiotics manufacture is second only to the production of alcoholic beverages as the major microbiological industry. The phenomenal rise of this industry during the past fifteen years has revolutionized industrial microbiology. Much of the story is well known. Nevertheless, it is worth recalling certain of the microbiological developments if only because they set a pattern for many of the advances that were to follow.

It is often assumed that the era of antibiotics dates from the observation by Alexander Fleming, in 1929, that a species of the mould *Penicillium*, growing on an agar plate seeded with pathogenic staphylococci, prevented growth of the bacteria by

D

excreting a substance which Fleming termed penicillin. But in fact, Pasteur had suggested the possibility of combating one microbe with another, and, as early as 1901, Emmerich and Low in the University of Munich had isolated a powerful germ-killing substance from the bacterium *Pseudomonas aeruginosa*, and had used it successfully in treating patients. But serious consideration of antibiotics as therapeutic agents only began around 1940, when a group of workers at Oxford, led by Howard Florey and Ernst Chain, set out to re-examine the production of penicillin. Wartime conditions naturally increased the importance of this study, but at the same time made progress rather difficult, so that in the summer of 1941 Florey and his colleague Heatley took the problem to the United States. There, a group of workers at the Northern Regional Research Laboratory, in Peoria, Illinois, developed the problem along three main lines. Firstly, the nutrient medium in which the mould was cultivated was modified by adding maize steep liquor and the milk sugar lactose, with the result that, when the mould was grown in this medium in submerged culture instead of as a green mat on the surface of the liquid medium, yields of penicillin were increased almost one hundredfold. Secondly, a search was made for other species and strains of *Penicillium* that were more efficient producers that Fleming's original strain of *P. notatum*. After a great deal of screening, a strain of *P. chrysogenum* was obtained that was capable of producing one and a half milligrams of pure penicillin in each millilitre of the fermentation medium. Finally, attention was directed to the chemical structure of penicillin. Analysis of the fermentation medium revealed the presence of several species of penicillin, all having the same structural nucleus or 'core', but differing in the nature of the side chain or 'tail' of the molecule. These penicillins had different antibiotic activities, with penicillin-G, or benzyl penicillin being on the whole most active against pathogenic bacteria. Further research showed that increased amounts of penicillin-G could be produced by feeding intermittently into the growing mould culture the substance phenyl acetic acid, which furnished ready-made the benzyl side-chain. This type of
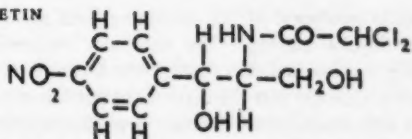
approach, using simultaneously nutritional, genetic, and bio-chemical studies, has since been successfully used in the develop-ment of other microbiological processes.

Throughout the 1930s, Selman A. Waksman of Rutgers Uni-versity in New Jersey, U.S.A., had been studying the actinomy-cetes that are found in soil. He had observed that many of these microbes had the ability to inhibit growth of other organisms, and in 1940 he succeeded in isolating the first antibiotic sub-stance produced by actinomycetes. This was termed actino-mycin : it had a powerful effect on several bacteria, but unfor-tunately was also toxic to animals. Four years later, however, Waksman and his students announced the isolation of another actinomycete antibiotic, called streptomycin, which not only acted against a wide range of disease-producing bacteria, but was relatively non-toxic.

The outstanding success of penicillin and streptomycin in treating infectious diseases sent industrial microbiologists searching feverishly for sources of other antibiotics. Thousands of microbes were screened for antibiotic-producing ability, special attention being given to soil micro-organisms. Airline pilots, missionaries, and explorers, all were asked to bring back soil samples from remote corners of the globe for examination : this was truly a return to the days of the Gold Rush. Success came quickly, for within a few years several clinically valuable antibiotics, including chloromycetin, aureomycin, and terra-mycin, were being produced in large quantities, all from soil micro-organisms. But only a score or so of the hundreds of anti-biotics that have since been isolated are manufactured on an industrial scale. Antibiotic production is now an extremely com-petitive industry, with an annual production of more than 1000 tons.

The search for new antibiotics continues, particularly for those active against the troublesome pathogenic fungi, viruses, and more recently, malignant cells. Increasing attention is also being devoted to more fundamental aspects of antibiosis, and in particular to ways in which antibiotics are synthesized, the mechanisms by which they act, and ways in which the molecule

can be modified chemically. As a result, the problem is becoming increasingly biochemical, although the microbiologist still has a vital role to play. This was well illustrated by the important discovery made recently by research workers of the Beecham group. It was found that, even after all the penicillin had been extracted from a fermentation medium, nevertheless

Formulae, sources, and uses of some important antibiotics

PENICILLIN

$$R = C_6H_5CH_2 = \text{penicillin-G}$$
$$R = CH_3CH_2CH = CHCH_2 = \text{penicillin-F}$$

Penicillin is produced by *Penicillium chrysogenum* and is used in treating staphylococcal infections, gas gangrene, anthrax, venereal diseases.

STREPTOMYCIN

Streptomycin is produced by *Streptomyces griseus* and is used in treating tuberculosis and tularemia.

CHLOROMYCETIN

Chloromycetin is produced by *Streptomyces venezuelae* and is used in treating intestinal diseases, e.g., typhoid and dysentery, and various forms of typhus.
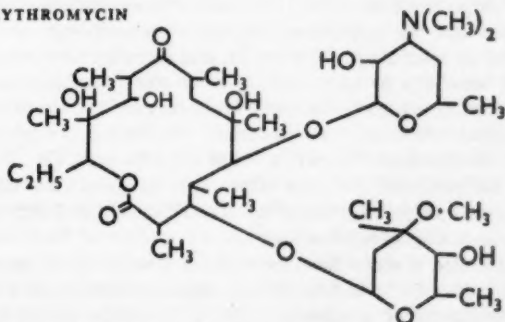
TETRACYCLINES
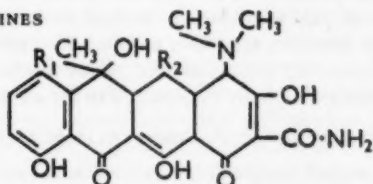
$R_1 = Cl, R_2 = H$. aureomycin
$R_1 = H, R_2 = OH$ terramycin

Tetracyclines are produced by *Streptomyces aureofaciens* and *S. rimosus* and are used in treating pulmonary infections, including viral pneumonia, and bacterial infections of digestive and urinary tracts.

ERYTHROMYCIN

Erythromycin is produced by *Streptomyces erythreus* and is used in treating typhus, and various bacterial diseases.

chemical treatment of the remaining fluid produced a further penicillin-like activity. The substance responsible for this activity was isolated, and shown to be 6-amino penicillanic acid, which is virtually just the core of the penicillin molecule, without a side chain. Now 6-amino penicillanic acid has no antibiotic activity of its own, but once it has been isolated, it can be passed to the biochemist who then attaches a suitable side chain to the molecule to give various species of penicillin. The great value of this discovery is that it makes possible the production of species of penicillin that can be used to combat strains of pathogenic microbes that have developed a resistance to the naturally occurring penicillins. Clearly, the biochemist's dream of tailor-made antibiotics may not be so far away.

RECENT ADVANCES IN INDUSTRIAL MICROBIOLOGY

The phenomenal success of antibiotics has been followed by a period of intense activity in other fields of industrial microbiology, one in which the trend has been increasingly towards using micro-organisms to manufacture comparatively small quantities of chemically complex substances. Again, these developments have required the close co-operation of the microbiologist and the biochemist. The geneticist too has an increasingly important role to play. The pioneer research on penicillin showed how the performance of micro-organisms can be improved by selecting suitable strains, and genetical studies have since been used to advantage in many other microbiological processes. One further outcome of this expansion of the microbiological industries is that an entirely new branch of engineering – biochemical engineering – has been formed. This deals with the problems that arise when micro-organisms are cultivated on a large scale, including the sterilization and aeration of large batches of nutrient media, and extraction of the various fermentation products from the medium. Biochemical engineering is now rapidly finding its way into the curricula of most chemical engineering schools.

Some idea of the scope of recent developments in industrial microbiology can be seen from the brief survey below.

Microbial food

According to a recent estimate, roughly two-thirds of the world's population are underfed. Not only are these hungry millions consuming insufficient quantities of food, but their diets are usually lacking in high quality protein and in certain essential vitamins. Largely under the auspices of the Food and Agriculture Organization of the U.N., considerable progress has already been made towards increasing world food production, including schemes for land reclamation and for more efficient use of crops. But some of the most interesting developments in recent years have been concerned with the use of microbes as a food for man and as a fodder for animals. For centuries, micro-organisms have been consumed in fermented foods and beverages, while mushrooms and truffles, which are simply the fruiting bodies of certain microscopic fungi, are well known gastronomic delicacies. But now, microbes are being considered as major sources of high quality protein and of B-group vitamins in human and animal diets.

In the manufacture of microbial food, it is clearly an advantage to select a microbe that will convert cheap raw material quickly and efficiently into new cell material. Photosynthetic micro-organisms would therefore appear to be ideally suited because, using simply atmospheric carbon dioxide and certain mineral elements, they can manufacture all of the constituents of living protoplasm. Some success has indeed been achieved employing green algae, particularly species of the quick-growing, unicellular alga, *Chlorella*. The Japanese, who for centuries have included seaweeds in their diets, have made considerable progress in this venture, due mainly to the efforts of Professor Tamiya in the University of Tokyo; moreover, Madam Tamiya has devised several recipes for using dried *Chlorella* in making bread, soups, and even ice cream. Unfortunately, the cost of manufacturing large quantities of algal food can be prohibitive, with special equipment being required for supplying the cultures with carbon dioxide and light, as well as for keeping them well stirred. However, the possibility of mass-culturing algae in

sewage has recently aroused considerable interest, and this may well provide a cheaper way of cultivating algal food.

The idea of employing yeast as a source of food was first suggested by the German microbiologist Delbruck, in a lecture 'Hefe, ein Edelpilz' ('Yeast, a Refined Fungus'). Most of the pioneer work on food yeast was carried out by German workers, but in 1943 the British Colonial Office set up a food yeast factory in Jamaica, largely in an attempt to find a use for the crude molasses that is a by-product of the sugar-refining industry. Since the war, several other food yeast factories have been built, notably in the United States and in Asia.

Yeast has for many years been propagated on a large scale for baking bread. But although baker's and brewer's yeasts have been used as food yeast, most plants now in operation cultivate the yeast *Candida utilis*. The nutritional value of the two species is almost identical, but *C. utilis* has the advantage of being able to utilize the pentose sugars that are commonly found in the wood hydrolysates and other raw materials used. Yeast protein does not, however, furnish all the essential amino acids that are required in human and animal nutrition – it is low in methionine – but with its high content of lysine, it serves as a valuable supplement to lysine-deficient vegetable protein. This, together with the high content of B-group vitamins, has led to food yeast being used extensively in parts of Central America, Africa, and Asia, both as a human food supplement and in animal fodder. Although one of the major obstacles to the more widespread use of food yeast is the problem of devising ways of incorporating the product into food in a palatable form, it is, without doubt, potentially a very valuable source of food in an undernourished world.

Although interest in microbial food centres largely around its value as a source of protein and of B vitamins, fat production by micro-organisms has for some years now attracted the attention of nutritional experts. Several microbial species, including the yeasts *Endomyces vernalis* and *Rhodotorula glutinis* and a wide variety of moulds, are known to synthesize large quantities of fat when cultivated under particular nutritional conditions.

During both world wars, microbial fat was widely used in Germany, but under normal circumstances it cannot compete in price with that produced from animal sources. But should it prove possible to manufacture a microbial fat with a high content of unsaturated fatty acids, then this might be very valuable in the prevention of arteriosclerosis.
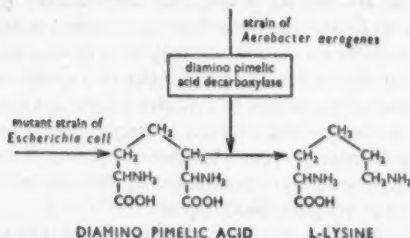
New fermentation products

The demand for pharmaceutical and biochemical products is being met increasingly by the microbiological industries. Vitamins are widely used as food supplements and in pharmaceutical preparations, and whereas most of these are made synthetically, a few are manufactured using micro-organisms. We have seen that many B-group vitamins function as coenzymes, but the amounts of a vitamin synthesized by a micro-organism are sometimes far in excess of those required for normal metabolic needs, with the result that large quantities are excreted. Thus riboflavin, or vitamin B_2, is obtained commercially from the yeastlike fungi *Eremothecium ashbyii* and *Ashbya gossypii*, the media in which these microbes are cultivated developing a deep yellow colour due to the large quantities of vitamin excreted. The anti-pernicious-anaemia factor, also known as vitamin B_{12}, is similarly produced using a species of *Streptomyces*; and, judging from the number of reports that have appeared in the literature recently, β-carotene, or provitamin A, will soon be obtained on a large scale from microbial sources.

Enzymes are finding ever-increasing uses in industries, especially in those concerned with food processing. They have several distinct advantages, particularly in view of their specific and non-toxic nature, and their ability to act under mild conditions of moderate temperature and near-neutral pH. Large numbers of microbial enzymes are employed, the majority of these being hydrolytic enzymes. Amylases, or starch-hydrolysing enzymes, obtained from species of fungi or from *Bacillus subtilis* strains, find a variety of applications, ranging from the desizing of textiles to the removal of wallpaper. The enzyme invertase, which is extracted from brewer's and baker's yeasts, is used to make

chocolate-coated, soft-centred sweets, and lactase from another species of yeast, *Saccharomyces fragilis*, prevents the milk sugar lactose from crystallizing out in ice-cream.

In recent years, several processes have been developed for the microbial production of amino acids. One amino acid now being manufactured in large quantities for use as a food supplement is lysine, which, as we have seen, is the essential amino acid that is generally lacking in vegetable protein. The method used for the commercial synthesis of this amino acid is particularly elegant. There are two main stages. In the first, a mutant strain of the bacterium *Escherichia coli* is grown in a medium containing glycerol, maize steep liquor, and various salts. The organism actually requires a small amount of lysine for growth, and it obtains this from the maize steep liquor, but whilst growing, it excretes considerable quantities of another amino acid, diamino pimelic acid. In the second stage, a closely related bacterium, *Aerobacter aerogenes*, is cultivated in a somewhat dif-

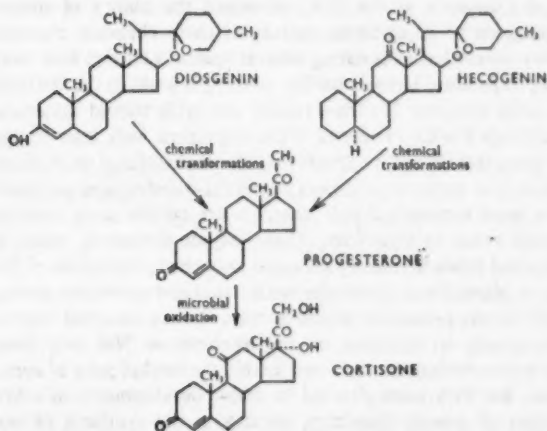DIAMINO PIMELIC ACID   L-LYSINE

ferent medium. This bacterium manufactures the enzyme diamino pimelic acid decarboxylase, and after toluene has been added to rupture the cells, the culture fluid is mixed with that from the mutant *E. coli* culture. On mixing, the diamino pimelic acid is enzymatically decarboxylated to give L-lysine, which is then recovered on ion-exchange columns. Lysine produced in this way is being used to fortify cereal foodstuffs.

Microbes as 'living reagents'

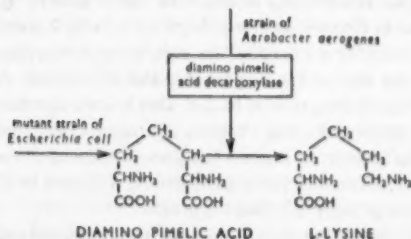Investigations into the biochemical activities of micro-organ-

isms have revealed the immense variety of chemical changes that can be brought about by these organisms. We have already seen that the enzymes responsible for these changes can often be isolated from the microbe in large quantity, but when the amount of enzyme produced is small, then it is often more convenient to use the growing micro-organism to bring about the desired change. In this way, microbes can be used to effect quite rapidly, and with consummate ease, chemical transformations that may involve the chemist in several separate steps. It is hardly surprising to find, therefore, that the chemist has enlisted the use of micro-organisms to help him synthesize a variety of industrially important compounds: essentially, he is using microbes as living reagents.

By far the most successful industrial application of micro-organisms in synthetic organic chemistry has been with steroid transformations. Considerable interest in the chemistry of steroids developed following the report that cortisone, a steroid from the adrenal glands, had the ability to relieve arthritic symptoms. However, the amounts that could be extracted from

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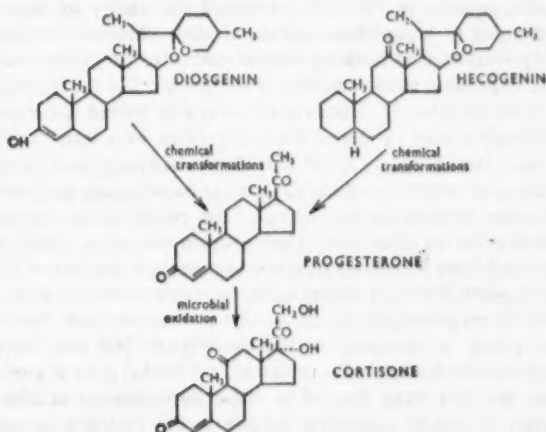DIAMINO PIMELIC ACID   L-LYSINE

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adrenal glands were very small indeed, at least 6,000 cattle being required to supply 100 milligrams of the steroid. A partial synthesis, starting with desoxycholic acid from cattle bile was later devised, although this required 37 separate chemical steps. When clinical trials were conducted with various steroids in order to obtain an insight into the chemical basis of cortisone action, it was found essential to have an oxygen atom in position 11 on the steroid nucleus to obtain biological activity. Unfortunately, the introduction of an oxygen atom into this position is a matter of considerable difficulty. Ten of the 37 steps in the synthesis starting from desoxycholic acid are required to shift the oxygen atom from position 12 to 11. While searching for some way of short-cutting this lengthy sequence of reactions, Durey Peterson and his colleagues of the Upjohn Pharmaceutical Company in the U.S., examined the ability of micro-organisms to bring about certain of these chemical changes. They succeeded in isolating several species of fungi that were able to produce steroids having an oxygen atom in the strategic position (number 11) from readily available steroid materials. Although a wide variety of micro-organisms were later shown to share this ability, it appears that filamentous fungi are the most active and versatile producers of steroid-transforming enzymes. The most economical raw materials are certain plant steroids which occur as glycosides. These include diosgenin, which is obtained from Mexican yams, and hecogenin, a product of the agave plant. These glycosides are isolated and converted chemically to progesterone, which in turn is then oxidized micro-biologically to cortisone or dihydrocortisone. Not only have these discoveries reduced considerably the market price of corti-sone, but they have also led to major developments in other realms of steroid chemistry, notably in the synthesis of sex hormones.

THE FUTURE

In this short article we have considered some of the wide range of products that are manufactured microbiologically. At the same time it has been possible to appreciate the enormous

chemical potentialities of micro-organisms, and the future will almost certainly see these chemical activities used increasingly in industrial processes. Clearly, much will depend upon demand, but for the next few years it is probably safe to say that progress will be greatest in processes concerned with the manufacture of food supplements and pharmaceuticals. Also, one can expect to see notable advances in microbial technology and, in particular, the development of continuous processes to replace batch methods still used in many microbial industries. But there can be little doubt that mankind will derive increasing benefits from this continued exploitation of the chemical activities of micro-organisms.

FURTHER READING

The standard texts on industrial microbiology are the two volumes *Industrial Fermentations*, edited by L. A. Underkofler and R. J. Hickey (New York, Chemical Publishing Co., 1954), and *Industrial Microbiology*, by S. C. Prescott and C. G. Dunn (New York, McGraw-Hill Book Co., Inc., 1959). Recent advances in the subject are dealt with in *Progress in Industrial Microbiology* Vol. 1, edited by D. J. D. Hockenhull (London, Heywood & Co. Ltd, 1959), and in a paper by J. J. H. Hastings, 'New Products of the Fermentation Industry', *Chemistry & Industry*, 1957 #274. Some idea of the scope of microbial technology can be found in *Biochemical Engineering*, edited by R. Steel (London, Heywood & Co. Ltd, 1958). And for those interested in the prospects for industrial microbiology in the year 2000, there is the winning entry, by M. B. McEvedy, in the Royal Society of Arts Bicentenary Essay Competition, and published in *Chemical Products*, 1955 **18** 141.

FREE RADICALS IN
COMBUSTION PROCESSES

L. C. ROSELAAR

ONE of the most fundamental properties of free atoms is their tendency to combine with each other. This explains why it is often difficult to obtain elements in their atomic form. For example, although it is possible to obtain nascent hydrogen, a reactive form of hydrogen gas which owes its activity to the fact that it contains a relatively large proportion of free hydrogen atoms, this does not remain active for very long because the atoms soon combine with each other to form molecules:

$$2H \!-\!\!= H_2$$
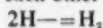
Atoms with unsatisfied valency bonds have in general only a fleeting existence. So, too, have free radicals, fragments formed

TABLE I.—*Some common free radicals.*

Name	Formula
Hydroxy	$HO-$
Peroxy	$HOO-$
Methyl	CH_3-
Methoxy	$CH_3.O-$

by breaking linkages in molecules, of which a few examples are given in Table I. These transient entities, however, play an important part as intermediates in chemical reactions. It is the purpose of this article to describe the role of free radicals in gaseous reactions in general, and in combustion processes in particular.

Reactions between gases and vapours can be studied in the laboratory if attention is paid to control of conditions such as the temperature and the respective partial pressures of the reacting gases. Over the years much empirical information has been collected concerning a number of reactions. For example, the now classical researches of Bodenstein (1899) have given us con-

siderable knowledge concerning the decomposition of hydrogen iodide into hydrogen and iodine; the reverse reaction was also studied:

$$2HI \rightleftharpoons H_2 + I_2$$

Another reaction, which has been extensively studied by Hinshelwood's school at Oxford, is the apparently 'simple' reaction between hydrogen and oxygen:

$$2H_2 + O_2 = 2H_2O$$

Of particular interest in connexion with free radicals is the hydrogen-chlorine reaction:

$$H_2 + Cl_2 = 2HCl$$
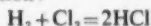
This is an example of a photochemical process, namely one that is set going not by the application of heat but by exposure of the reacting gases to light. A final example, this time from the organic field, is the decomposition under the influence of heat, or pyrolysis, of acetaldehyde ($CH_3.CHO$) which decomposes to give methane and carbon monoxide:

$$CH_3.CHO = CH_4 + CO$$

The results that can be obtained are of two types, kinetic and analytical. Kinetic results show how the rate of reaction depends on various factors such as temperature, total pressure of reacting gases, relative amounts of reacting gases, and so on. The rate of reaction is usually measured by following the change in some variable. Thus in the pyrolysis of acetaldehyde, since two molecules are produced from one, there is an expansion which, if the gases are kept in a confined space, manifests itself as an increase in pressure. It is found that, under certain conditions, the rate of pressure increase is directly proportional to the square of the partial pressure of the acetaldehyde vapour. This is a typical kinetic result and it means that the rate is proportional to the concentration of acetaldehyde squared.

Analytical results show what happens to the reacting gases; the reaction products are analysed chemically at certain intervals during the reaction. Figure 1 illustrates analytical results for the reaction at 196° C between acetaldehyde ($CH_3.CHO$) and oxygen. It is difficult to represent this reaction by means of a simple chemical equation because the products are numerous.

TIME

Oxidation of Acetaldehyde
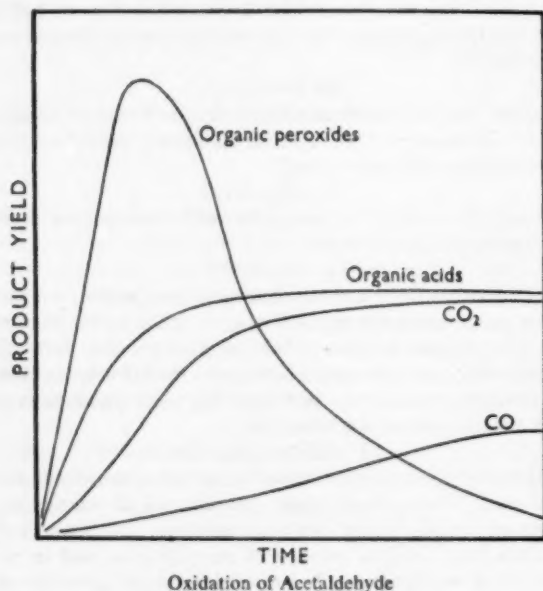
However, the diagram shows that during the course of reaction (which takes about seven minutes) carbon dioxide and various organic acids (chiefly acetic acid, $CH_3.CO.OH$, and peracetic acid, $CH_3.CO.OOH$) build up, and there is also a certain amount of carbon monoxide. Organic peroxides (compounds having the peroxide grouping —O—O— in the molecule) are formed to a large extent at first, but are soon used up. These peroxides are therefore regarded as intermediates in the reaction.

At one time it was believed that reactions were the direct consequence of collisions between molecules. It is, indeed, easy to build up a picture of the mechanism whereby hydrogen iodide decomposes. Two molecules of hydrogen iodide come together and an interchange of bonds takes place:

$$\begin{matrix} H & H \\ | & | \\ I & I \end{matrix} \longrightarrow \begin{matrix} H{-}H \\ \\ I{-}I \end{matrix}$$
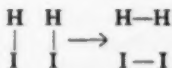
but a similar picture for other reactions is more difficult to visualize. For example, in the hydrogen-oxygen reaction it would be necessary for two molecules of hydrogen to collide at one and the same time with a molecule of oxygen. Triple collisions in the gas phase are comparatively rare, but even if a suitable triple collision did occur it would be difficult to imagine the molecules orientating themselves in such a way that the interchange of the various atoms could easily take place.

The present tendency is to regard many reactions as involving a series of simple steps. These individual steps usually involve free radicals. The earliest free-radical mechanism was postulated by Nernst (1918) to explain the hydrogen-chlorine reaction. The amount of light absorbed in this reaction is very small and Nernst suggested that its function is only to initiate the reaction by splitting a few molecules of chlorine into free atoms:

$$Cl_2 + light \longrightarrow 2Cl- \qquad (1)$$

A free chlorine atom then reacts with a molecule of hydrogen, producing a new molecule of hydrogen chloride and a free hydrogen atom:

$$Cl- + H_2 \longrightarrow HCl + H- \qquad (2)$$
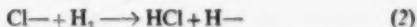
The latter then reacts with a molecule of chlorine producing a second hydrogen chloride molecule and a free chlorine atom which can react as in (2) above:

$$H- + Cl_2 \longrightarrow HCl + Cl- \qquad (3)$$
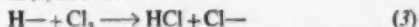
In this way steps (2) and (3) occur again and again in a chain and many molecules of hydrogen chloride are produced as the result of the absorption of a very small amount of light energy. The chain only comes to an end on those rare occasions when two free atoms meet and combine. The following three combinations will stop two chains:

$$H- + H- \longrightarrow H_2 \qquad (4)$$
$$Cl- + Cl- \longrightarrow Cl_2 \qquad (4a)$$
$$H- + Cl- \longrightarrow HCl \qquad (4b)$$

and are called chain-terminating steps.

Evidence of a more direct nature for the existence of free radicals was obtained by Paneth and Hofeditz (1929). A simple diagram of their apparatus is shown in Figure 2. The vapour of lead tetramethyl ($Pb(CH_3)_4$) was passed through a quartz tube. At a certain point along the tube they heated it, and they found that a shiny 'mirror' of lead was formed just beyond the point of heating. Then they heated the tube at another point further upstream. Once again a lead mirror was deposited just beyond the point of heating and, this time, the first mirror, which had already been formed lower down the tube, began to be gradually eaten away. Paneth and Hofeditz explained these results by the
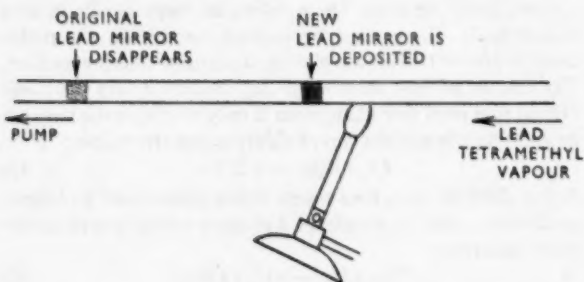

suggestion that at high temperatures lead tetramethyl breaks up into metallic lead and free methyl radicals:

$$Pb(CH_3)_4 \longrightarrow Pb + 4CH_3— \qquad (1)$$

The free methyl radicals would normally be expected to combine with each other to produce ethane:

$$2CH_3— \longrightarrow CH_3.CH_3 \qquad (2)$$
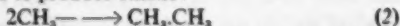
but if before doing so they come across metallic lead at a lower temperature they will recombine with it to form lead tetramethyl:

$$Pb + 4CH_3— \longrightarrow Pb(CH_3)_4 \qquad (3)$$
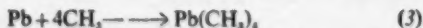
Later work has shown that many other organic compounds decompose to give free radicals that can eat up mirrors, not only of lead, but also of other metals, such as antimony, tellurium,

and zinc. For example, when nitroethane ($C_2H_5.NO_2$) is heated it breaks up into nitrogen peroxide (NO_2), which has been isolated, and an ethyl radical:

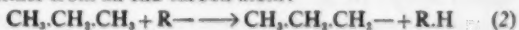$$C_2H_5.NO_2 \longrightarrow C_2H_5- + NO_2 \qquad (1)$$

The evidence for the production of ethyl radicals is that a mirror of tellurium can be removed and that there is produced an evil-smelling compound which is identified as diethyl ditelluride ($C_2H_5.Te.Te.C_2H_5$):

$$C_2H_5- + 2Te \longrightarrow C_2H_5.Te.Te.C_2H_5 \qquad (2)$$

With this evidence in mind, Rice (1932) proposed free radical mechanisms as being operative in the thermal decomposition of many hydrocarbons and hydrocarbon derivatives. Thus, when propane ($CH_3CH_2.CH_3$) is heated it breaks down into three main products: propylene ($CH_3.CH=CH_2$), ethylene ($CH_2=CH_2$), and hydrogen. There is no simple equation representing this process. Rice suggested that a molecule of propane first splits under the action of heat to form an ethyl and a methyl radical:

$$CH_3.CH_2.CH_3 \longrightarrow CH_3.CH_2- + CH_3- \qquad (1)$$
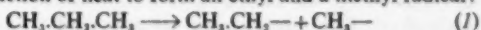
These radicals (denoted by R—) can react with another propane molecule by combining with a hydrogen atom and forming ethane or methane. The propane molecule can lose its hydrogen atom either from an end carbon atom:

$$CH_3.CH_2.CH_3 + R \longrightarrow CH_3.CH_2.CH_2- + R.H \qquad (2)$$

or from the centre:

$$CH_3.CH_2.CH_3 + R \longrightarrow CH_3.CH:CH_3 + R.H \qquad (2a)$$

The formation of double-bond compounds is easily understood because the free radical formed in step (2) can split up into a methyl radical and ethylene ($CH_2=CH_2$):

$$CH_3.CH_2.CH_2- \longrightarrow CH_3- + CH_2=CH_2 \qquad (3)$$
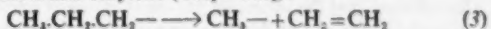
and that formed in step (2a) can split up forming propylene ($CH_3.CH=CH_2$) and a free hydrogen atom:

$$CH_3.CH.CH_3 \longrightarrow CH_3.CH=CH_2 + H- \qquad (3a)$$
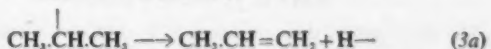
If the hydrogen atom is now substituted for a free radical (R—) in steps (2) and (2a) the production of molecular hydrogen is explained.

COMBUSTION REACTIONS

At present much interest is being shown in the mechanism of reaction between oxygen and various organic compounds. This interest has arisen particularly from the desire to gain more information regarding combustion. Petroleum fuels consist largely of paraffin hydrocarbons. These burn with evolution of heat to gaseous products which, because of this heat, are made to expand, and in the internal combustion engine this expansion is made to move a piston. The heat is thus converted into work and the problem is to produce the maximum work from the smallest amount of fuel.

Since the internal combustion engine was first developed much information has been collected regarding the optimum conditions for its operation, and, as a result, its efficiency has been increased considerably. However, most of the knowledge obtained so far has been empirical knowledge, and it is now realized that if further advances are to be made, it will be necessary to have a clearer understanding of the basis of combustion processes, i.e., of the molecular and free radical mechanism underlying the overall reactions. It is for this reason that attention is being paid in the laboratory to the reactions between oxygen and various organic compounds, such as paraffin hydrocarbons and alcohols.

The gaseous oxidation, or autoxidation, of paraffin hydrocarbons was shown analytically to involve organic peroxides (R.OOH) as intermediates, the final products including alcohols (R.OH), aldehydes (R.CHO), and carbon monoxide. It is generally believed that the initial step is the reaction of a hydrocarbon molecule with a molecule of oxygen to produce an alkyl radical and a peroxy radical (HOO—):

$$R.H + O_2 \longrightarrow R— + HOO— \qquad (1)$$

The alkyl radical then combines with another molecule of oxygen to form an alkyl peroxy radical (R.OO—):
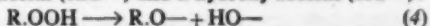
$$R— + O_2 \longrightarrow R.OO— \qquad (2)$$

This then reacts with a parent hydrocarbon molecule giving an

alkyl peroxide (R.OOH) and another alkyl radical which will continue the chain:

$$R.OO— + R.H \longrightarrow R.OOH + R— \qquad (3)$$

The alkyl peroxide (R.OOH) is very unstable and decomposes into an alkoxy radical (R.O—) and a hydroxy radical (HO—):

$$R.OOH \longrightarrow R.O— + HO— \qquad (4)$$

The subsequent reactions of the peroxy (HOO—), hydroxy (HO—), and alkoxy (R.O—) radicals will depend upon the conditions under which the reaction occurs; they will, of course, include chain-ending reactions.

It should be noted that the alkyl radical produced in step (*1*) reacts to produce three radicals, namely another alkyl radical (R—) in (*3*), as well as a hydroxy radical and an alkoxy radical in (*4*). This multiplication of free radicals, or chain branching, causes the reaction to become faster and faster. In a system where chain branching greatly exceeds chain-ending, explosion can occur. The phenomenon of 'engine knock' is also believed to be connected with chain branching. The reason for 'knock' is still not completely understood, but it is probably due to the combustion reaction getting too fast for the engine.

The above mechanism is supported by work on other reactions where there has been more certainty about the radicals involved. In the remainder of this article an account is given of some of these reactions, and the light that they throw on the chemistry of the following organic free radicals:
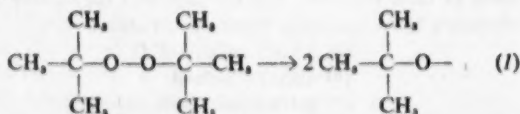
        (*a*) alkoxy radicals (R.O—)
        (*b*) alkyl radicals (R—)
        (*c*) peroxy radicals (R.OO—)
        (*d*) acyl radicals (R.CO—)

In general, when one of these radicals is in the presence of molecules of oxygen and of an organic substance, three types of reaction are possible – in addition to chain-terminating reactions. The first type of reaction is decomposition; the radical may split up into another radical and a stable molecule. Examples of free radical decomposition are steps (*3*) and (*3a*) in the mechanism given above for the decomposition of propane ($CH_3.CH_2.CH_3$). The second type of free-radical reaction is

hydrogen abstraction in which the radical removes a hydrogen atom from another molecule, stabilizing itself but producing a new free radical. This possibility is illustrated by step (2) in the hydrogen-chlorine reaction, by (2) and (2a) in the mechanism for propane ($CH_3.CH_2.CH_3$) decomposition, and by (3) in the autoxidation scheme. Finally, the free radical can undergo reaction with a molecule of oxygen. Step (2) in the autoxidation mechanism shows the beginning of such a process.

The alkoxy radical (R.O—)

In the autoxidation mechanism an alkoxy radical (R.O—) is produced in step (4). A knowledge of its subsequent fate is clearly desirable as we shall then be able to account for the final products of combustion. This knowledge has been provided largely as the result of work by Vaughan's school in California. These workers carried out some interesting work on the thermal decomposition of di-tertiary butyl peroxide (($(CH_3)_3C.O.O.C.(CH_3)_3$). Chemical analysis showed that the main products of this reaction were acetone ($CH_3.CO.CH_3$) and ethane ($CH_3.CH_3$). The following mechanism was therefore proposed. It was suggested that the peroxide molecule first breaks up by splitting at the centre (O—O) bond into two tertiary butoxy radicals (($(CH_3)_3C.O$—):

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow 2\,CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O- \qquad (1)$$

The tertiary butoxy radical then decomposes by losing a methyl radical to form acetone ($CH_3.CO.CH_3$):

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O- \longrightarrow CH_3- + \underset{\underset{CH_3}{|}}{\overset{}{C}}=O \qquad (2)$$
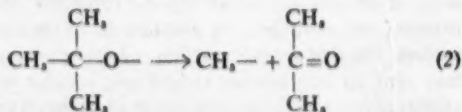
This second step seems to occur very readily. The methyl radical so produced seems to be incapable of removing a hydrogen

atom from another molecule as it apparently waits until it can pair up with another methyl radical to form ethane.

Not all alkoxy radicals show as much instability as the butoxy radical. Results given below indicate that the methoxy radical $(CH_3.O—)$ is quite stable and, instead of decomposing, abstracts a hydrogen atom from a molecule to form methyl alcohol $(CH_3.OH)$.

The alkyl radical (R—)

Of the alkyl radicals (R—), most work has been done on the first two in the series, methyl and ethyl. It was shown above that the tertiary butoxy radical $((CH_3)_3.C.O—)$ decomposes to give a methyl radical, and therefore a convenient method for studying the reactions of the latter was to heat di-tertiary butyl peroxide $((CH_3)_3.C.O.O.C(CH_3)_3)$ in presence of oxygen. When the products were analysed it was found that, in addition to acetone, large quantities of methyl alcohol $(CH_3.OH)$ were present and this was therefore regarded as the main oxidation product of the methyl radical. The reaction scheme suggested is essentially the same as that incorporated in the general mechanism for the oxidation of paraffin hydrocarbons already given. The methyl radical is regarded as combining with a molecule of oxygen to give a methyl peroxy radical:

$$CH_3— + O_2 \longrightarrow CH_3.OO— \qquad (1)$$
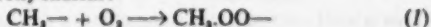
This then abstracts a hydrogen atom from a molecule giving methyl peroxide $(CH_3.OOH)$:

$$CH_3.OO— + R.H \longrightarrow CH_3.OOH + R— \qquad (2)$$

This is a very unstable compound which readily splits up, forming a methoxy radical $(CH_3.O—)$ and a hydroxy radical $(HO—)$:

$$CH_3.OOH \longrightarrow CH_3.O— + HO— \qquad (3)$$
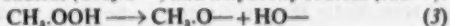
and the large yield of methyl alcohol $(CH_3.OH)$ is the reason for believing that the main reaction of the methoxy radical is hydrogen abstraction to form this compound:

$$CH_3.O— + R.H \longrightarrow CH_3.OH + R— \qquad (4)$$
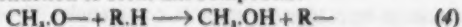
A similar series of reactions is undergone by the ethyl radical $(CH_3.CH_2—)$. The reaction of this radical with oxygen was studied by allowing ethane $(CH_3.CH_3)$ and oxygen to react in

presence of hydrogen bromide (HBr) which acts as a catalyst. The major oxidation product was found by analysis to be acetic acid ($CH_3.CO.OH$). Hydrogen bromide is unstable and will break up on heating to form two chain-initiators, an atom of hydrogen and one of bromine:

$$HBr \longrightarrow H-\ +\ Br- \qquad (1)$$

Either of these can then abstract a hydrogen atom from an ethane molecule ($CH_3.CH_3$) so that an ethyl radical ($CH_3.CH_2-$) is formed:

$$CH_3.CH_3 + R- \longrightarrow CH_3.CH_2- + R.H \qquad (2)$$

This ethyl radical ($CH_3.CH_2-$) then undergoes reaction with oxygen to given an ethyl peroxy radical ($CH_3.CH_2.OO-$):

$$CH_3.CH_2- + O_2 \longrightarrow CH_3.CH_2.OO- \qquad (3)$$
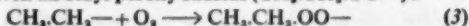
which abstracts a hydrogen atom forming ethyl peroxide ($CH_3.CH_3.OOH$):

$$CH_3.CH_2.OO- + R.H \longrightarrow CH_3.CH_2.OOH + R- \qquad (4)$$
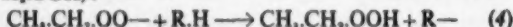
As before, the peroxide molecule ($CH_3.CH_2.OOH$) is very unstable and undergoes decomposition to give an ethoxy radical ($CH_3.CH_2.O-$) and a hydroxy radical:

$$CH_3.CH_2.OOH \longrightarrow CH_3.CH_2.O- + HO- \qquad (5)$$
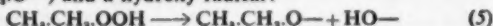
The ethoxy radical ($CH_3.CH_2.O-$) presumably decomposes to form acetaldehyde ($CH_3.CHO$):

$$CH_3.CH_2.O- \longrightarrow CH_3.CHO + H- \qquad (6)$$

This is itself oxidized, also by a peroxidic mechanism (see below) to acetic acid ($CH_3.CO.OH$):

$$CH_3.CHO \xrightarrow{\text{oxidation}} CH_3.CO.OH \qquad (7)$$
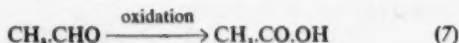
The peroxy radical (R.OO—)

Now, so far, the participation in the above reaction schemes of peroxy radicals has been tacitly assumed, although methyl peroxide ($CH_3.OOH$) and ethyl peroxide ($CH_3.CH_2.OOH$) have never been detected as intermediates in the above reactions; they seem to be extremely unstable compounds. There is, however, one case in which Vaughan and his co-workers were able to isolate a peroxide. This was the autoxidation of tertiary butane (($CH_3)_3CH$) in the presence of hydrogen bromide; tertiary butyl

peroxide ((CH_3)$_3$C.O.OH) was produced. The following mechanism was therefore suggested. The tertiary butyl radical ((CH_3)$_3$C—) is produced as the result of hydrogen abstraction by a free radical:

$$(CH_3)_3CH + R— \longrightarrow (CH_3)_3C— + R.H \qquad (1)$$

This reacts with oxygen to form the tertiary butyl peroxy radical ((CH_3)$_3$C.OO—):

$$(CH_3)_3C— + O_2 \longrightarrow (CH_3)_3C.OO— \qquad (2)$$

which forms tertiary butyl peroxide ((CH_3)$_3$C.OOH) by hydrogen abstraction:

$$(CH_3)_3C.OO— + R.H \longrightarrow (CH_3)_3C.OOH + R— \qquad (3)$$
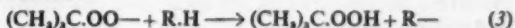
Here, then, is positive evidence for the peroxidic mechanism.

The acyl radical (R.CO—)

It has been shown above that the tertiary butoxy radical ((CH_3)$_3$C.O—) decomposes to give acetone (CH_3.CO.CH_3), and the ethoxy radical (CH_3.CH_2.O—) decomposes to yield acetaldehyde (CH_3.CHO). The oxidation of aldehydes (R.CHO) and ketones (R.CO.R′) is therefore of interest, as they are important intermediates in fuel combustion. Information regarding the free radicals which can be derived from these compounds is still being built up. The reactions of the acetyl radical (CH_3.CO—), however, are now fairly clearly understood; they have been obtained from studies on reactions of acetaldehyde (CH_3.CHO). This compound decomposes on heating to give methane and carbon monoxide:

$$CH_3.CHO = CH_4 + CO$$

The nature of the products has been explained on the assumption that the molecule (CH_3.CHO) first decomposes to form an acetyl radical (CH_3.CO—) and a hydrogen atom:

$$CH_3.CHO \longrightarrow CH_3.CO— + H— \qquad (1)$$
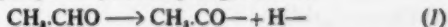
The acetyl radical (CH_3.CO—) then undergoes decomposition to a methyl radical and carbon monoxide:

$$CH_3.CO— \longrightarrow CH_3— + CO \qquad (2)$$

The methyl radical abstracts a hydrogen atom from a parent

molecule; in this way methane and another acetyl radical are formed and the chain is continued:

$$CH_3.CHO + CH_3 \longrightarrow CH_4 + CH_3.CO— \quad (3)$$

The autoxidation of acetaldehyde occurs at a much lower temperature than the thermal decomposition. This ease of reaction is believed to result from the readiness with which a molecule of oxygen removes a hydrogen atom from a parent molecule. The products of this reaction are an acetyl radical and a peroxy radical:

$$CH_3.CHO + O_2 \longrightarrow CH_3.CO— + HOO— \quad (1)$$
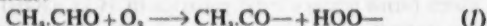
As before the acetyl radical can decompose to a methyl radical and carbon monoxide:

$$CH_3.CO— \longrightarrow CH_3— + CO \quad (2a)$$

This time the methyl radical will react with oxygen, by the mechanism described above, to give methyl alcohol:

$$CH_3— \xrightarrow{\text{oxidation}} CH_3.OH \quad (3a)$$
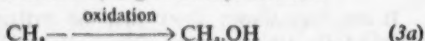
This is, indeed, one of the products found. The acetyl radical can also react with oxygen to produce a peroxy acetyl or peracetyl radical $(CH_3.CO.OO—)$:

$$CH_3.CO— + O_2 \longrightarrow CH_3.CO.OO— \quad (2b)$$
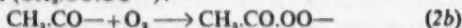
which will abstract a hydrogen atom to give peroxy acetic or peracetic acid $(CH_3.CO.OOH)$:

$$CH_3.C{\overset{\textstyle O}{\underset{\textstyle O.O—}{\big|}}} + R.H \longrightarrow CH_3.C{\overset{\textstyle O}{\underset{\textstyle O.OH}{\big|}}} + R— \quad (3b)$$
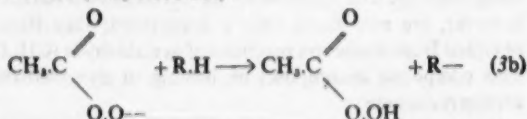
Large quantities of peracetic acid $(CH_3.CO.OOH)$ are found at lower temperatures. At higher temperatures the yield is somewhat less. It appears that the peracetic acid $(CH_3.CO.OOH)$ breaks up, like other organic peroxides, giving a hydroxy radical and an acetic radical:

$$CH_3.C{\overset{\textstyle O}{\underset{\textstyle O.OH}{\big|}}} \longrightarrow CH_3.C{\overset{\textstyle O}{\underset{\textstyle O—}{\big|}}} + HO— \quad (4b)$$
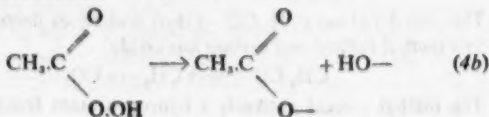
The acetic radical can also abstract a hydrogen atom forming acetic acid:

$$CH_3.C\begin{matrix} O \\ \diagup \\ \diagdown \\ O- \end{matrix} + R.H \longrightarrow CH_3.C\begin{matrix} O \\ \diagup \\ \diagdown \\ OH \end{matrix} + R- \qquad (5b)$$
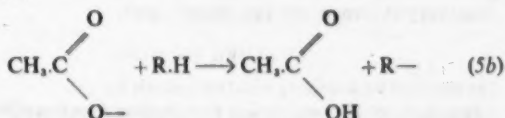
This is the mechanism for the production of acetic acid in the oxidation of ethyl radicals. Another product of this reaction is carbon dioxide which presumably results from decomposition of the acetic radical:

$$CH_3.C\begin{matrix} O \\ \diagup \\ \diagdown \\ O- \end{matrix} \longrightarrow CH_3- + CO_2 \qquad (6c)$$
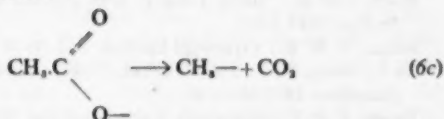
The methyl radical so produced is then oxidized to methyl alcohol (3a).

CONCLUSION

In this article it has not been possible to quote more than a few examples of gaseous reactions, the study of which has yielded information regarding the behaviour of free radicals. The reactions described were fairly unambiguous; it would be difficult to suggest any mechanisms alternative to those given. For this reason we can conclude that the general autoxidation scheme on page 92 is supported by good evidence.

The sceptic might suggest that, although this evidence is good, it is, nevertheless, 'indirect'; because, except possibly in the experiments of Paneth and Hofeditz, the free radicals were only detected at second-hand and their presence was postulated to fit the results. It is therefore satisfactory to know that during the last few years there have been developed a number of techniques, such as mass spectrometry and flash photolysis, which have made it possible to detect free radicals directly, and also to measure their concentrations. The applications of these techniques are necessarily still limited, but the results that have been

obtained suggest that the reaction mechanisms, such as those given in this article, which have been built up on the basis of secondary evidence, are the correct ones.

FURTHER READING

The standard book dealing with free radicals is:

Steacie, E. W. R.: *Atomic and Free Radical Reactions* (New York, Reinhold Publishing Corp., 1954).

Other general references are:

Trotman-Dickenson, A. F.: *Free Radicals: An Introduction* (London, Methuen, 1959).

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SOCIOLOGY FROM THE AIR

L. SILBERMAN

ARCHAEOLOGY is the oldest of the air–social sciences. Hence archaeologists are distinguishing precisely, even in the titles of their books, the digging part from other techniques – *Archaeology from the Earth*, as Sir Mortimer Wheeler's recent book is called, contrasts with *Discovery from the Air*, which is Major Allen's title for a well-known book of his. As far as aerial surveying is concerned, the classical text-book on the uses of the aeroplane to the archaeologist appeared as long ago as 1929. It was by the man who first developed it as a hobby during the First World War, and was O. G. S. Crawford's *Air Photography for Archaeologists*.

The reason for the association lies in the fact that since the latter part of the First World War soldiers have flown, especially in the Middle East, and that the soldiers there were often amateur archaeologists. An interest in fortifications, the possibilities of a landscape for the deployment of human ingenuity, the interpenetration of different peoples in the same physical space, may account for their admirable contributions. Different vegetational cover and changes in soil coloration which can easily be detected from the air, provide to the observant eye tell-tale indications of former sites. It is rare that a region is photographed without some new archaeological discovery being made. However, discovery is only part of air archaeology. Stereoscopic examination allows precise measurements to be taken, where, in the field, there is often no time or, in the scorching heat and thick bush, little inclination to do so. The developer of the stereoscope, Oliver Wendell Holmes, the sage of the U.S. Supreme Court, wrote about it in 1875: 'We are looking into stereoscopes now as pretty toys and wondering over this novelty, but before another generation has passed away it will be recognized that a new epoch has started in the history of human pro-

gress.' As he lived to 85 years, he was able, as far as archaeo-
logical studies were concerned, to see his optimism vindicated.

One essential aspect of measurement is counting. General Pitt
Rivers coined the slogan for archaeologists: 'Distribution is the
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the East Coast of Africa where the distribution of Arab and
Persian settlements still has to be carefully studied. The visible
remains of the various colonizing peoples – mosques, forts,
graves, and houses – can further be identified by a study of the
tribal histories and customs of peoples still living in the vicinity,
that is by 'ground control' which prompts the living to give us
clues about the characteristics of the dead. A combination of
air and social surveys is a natural development and the term
'sociogrammetry' might be applied to all the cross-checking
procedures.

CURRENT AIR SOCIAL RESEARCHES

If, by looking at aerial surveys and the types of rock outcrops
and the vegetation they show up, the photogeologist can indicate
what is underneath the Earth; if seaweed studies and infrared
photography of lakes and coastal shelves reveal sunken ships
and cities; if the plant ecologist and irrigation engineer can use
photogrammetry for locational research and planning, and in
the definition of drainage areas, land forms and meteorological
changes, then surely the social student can find many uses of his
own for the photo-interpretation of social relationships – human
activities that leave their imprint on the landscape.

Let me give some examples where air photography is already a standard procedure in social studies. Census work, especially in large countries that are air-minded such as North and South America, is an obvious starting point. The U.S. Bureau of the Census regularly calls for air photography and trains its staff in its interpretation. The more detailed sample inquiries, cutting out blocks from cities and in rural divisions, for which the Bureau has become internationally famous, are partially based on cluster sampling by air photography. In South America, Columbia, where people take air journeys as Europeans take overland buses, has made considerable use of air photography. The census authorities there count human habitations as recorded from the air and multiply them by the average number of occupants associated with each type of residence. This is already a step beyond the Liberian census which only counted residences without estimating their inhabitants, or for that matter the enumeration of nomads from the air, undertaken by the Palestine Government in the days of the British Mandate. In the ecological field counts of seals, salmon, or deer have often been made from the air, and game reserve policies are guided by this evidence. The size of nomadic groups and their stock is of prime importance to the administrator trying to minimize over-grazing and friction around wells.

The use of air photographs to make crop estimates for cotton or jute, the quantity of which can easily be estimated from the air long before it is reaped, directed the attention of the U.S. Department of Agriculture to the use of air photography as a basis for tax collection and the award of subsidies. Since 1936 the agricultural areas of the United States have been photographed annually as part of the programme designed to compensate the farmer for not overproducing certain commodities. The enormous number of photographs that have piled up in Washington as a result of this work are threatened with destruction, but now that their use for manifold rural studies is gradually being appreciated this historical material may still be saved.

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routine in preliminary studies made before master plans are draughted for each urban project. Ordinary maps are abstractions which often do not contain the specific information the planner wants, or overlays with specific data that are best studied against a background of air photography. The London County Council has commissioned air photographic surveys before making decisions on slum clearance or on urban sprawl.

In Paris, Los Angeles, in fact in most modern cities, traffic studies are now made by helicopters. The speed of cars can be measured stereoscopically. By the amount of apparent elevation a car has from the road the pace can be gauged with an accuracy of plus or minus five miles.

In urban studies a new approach has been made by the Chicago Aerial Survey where it has been used to estimate conversions in occupancy and through forward studies to judge the speed of erection and number of new residences built in a given area. The size of the house, the presence of television aerials, utility lines, garages, the condition of the yard and the street, give a good picture of the socio-economic group living in a neighbourhood if, through knowledge of the ground, a 'key' can be worked out for a built-up area that identifies the various features and allows them to be totalled. Investigating parts of Chicago for two utility companies, the company's photo-interpreters were able to 'visit' each building in 15 seconds. The error made in averaging the number of families living in each type of house was in this case, when checked on the ground, only 5 per cent. Field workers are usually wrong by the same margin because of dwellings units overlooked or data wrongly recorded.

The second study adds significantly to the usual historical information that can be derived by a retrospective analysis of past photographs. Knowing something of the propensities of the builders and the demand for particular types of dwellings, the investigators were able to forecast rates of future development. 1949 was taken as the base year with 882 residences. If subsequently the same types of buildings were erected, 2,547 could be fitted into the area under study. A second check in 1955 pro-

vided a means of predicting growth rates. By 1958 the amount of coverage differed from that predicted only by an insignificant difference. The number of dwelling units was also almost identical with the prediction. The same kind of projections can be made for petrol stations, shops, gardens; and any thoughtful large concern planning for future expansion will increasingly fit such studies into its business.

New experiments are not limited to North America. The Pan-American Union's training courses run in Brazil teach students not only to evaluate natural resources, but also to produce indices of social change, as shown through variations between different years and places, in density, quality, and type of structure, ploughing methods, and productivity. During the course of this year work will be concentrated on Ecuador. Likewise, as part of the Colombo Plan, the Hunting group of companies, among others, have made inventories of natural resources and improvements effected in cleared land. In Ceylon, Pakistan, and elsewhere, soil conservation, paddy-land improvement, hydrological programmes, flood control, pollution abatement, land use studies, and the reservation of suitable areas for airports or factory plants, community centres, and schools are facets of inter-related planning and mapping work that are being increasingly given a statistical dimension. In South Africa, as in other African countries, the farmer can purchase from the Government at subsidized rates air photographs together with technical advice on how better to plan his farm and fields in order to achieve higher yields without danger to the land. The next step is to evaluate the competence of the advice and then go on to measure the success of its implementation by individual farmers.

In Britain's old African possession, the Gambia, the Directorate of Overseas Surveys, one of the largest air survey units in the world, made a comparative study of air photographs taken in 1946 and again in 1956. Their aim was to establish the effectiveness of the Government's rice cultivation programme. Agitated debates in the legislature had queried the claim that more rice was being grown. Not only was the controversy

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cleared up by a factual account of the amount of rice being cultivated (much of which is consumed locally by the producer) but the suitability of different areas for rice growing was studied with the aid of photographs. If further guidance were needed, one could isolate whatever factors contributed most (and according to their cost optimally) to the programme.

When 'villagization' is next studied in Kenya, the lessons of the Gambia, Ecuador, and Chicago can be drawn upon. Before colonial rule the Kikuyu lived in villages as a means of protecting themselves against the Masai. With British rule came peace and at the same time a dispersal of the people who preferred to live close to their banana patches or maize fields so as to keep an eye on them. Mau Mau forced revillagization; with its many tragedies, the emergency also made more rational planning of the land possible, encouraged social services for the grouped villagers, and better marketing opportunities. The villages were, however, often planned without any regard to class differences and the diverging standards of the occupants, so there may be now a tendency to disperse unless constructive action is taken as suggested by a combined air and ground analysis.

THE METHOD OF AIR-SOCIAL STUDIES

Sociogrammetry – the marriage of social surveys, anthropological and economic field studies with photogrammetry – centres on three major problems.

First, it is a device to generalize, as well as to particularize, statistical data. Where national or regional figures exist collected on the ground, the air photograph gives details for a specific locality and shows how these local statistics correlate with other natural features of the landscape and social life; where only local data are available, the air photograph extrapolates the sample to similarly constituted areas with similar populations. Where the summarizing figures aggregate, the analysis of the sociogrammetrist disaggregates; where, on the other hand, relatively isolated disparate facts are all that are at our disposal, the air-social survey aggregates them with other similarly observable phenomena. Where the field enumerator's work is personal,

the photo-interpreter's is impersonal, and can be performed thousands of miles away.

Secondly, sociogrammetry gives to social science a new stimulus to examine the spatial dimension – how man fits himself into a terrain; what potential amenities he neglects and why; what conflicting uses of the spatial dimension lead to different forms of social malaise and even to strife as populations grow and become more differentiated. After many years of concentration on questionnaire studies, interviewer bias, sampling errors, the wording and sequence of questions, sociology becomes once more visual. Often the ecological rearrangements, objectively shown in successive photographic surveys, when coupled with ground studies, give more telling pictures of change than do opinion studies. With all the difficulties of quantifying qualified statements intelligently, or making field observations, with all the danger of noticing only the dramatic and neglecting the commonplace, more revealing things become less consciously controlled. When we have a fairly complete air–social study of present-day circumstances in an area, a historical air survey alone can help us to judge how successfully the people have advanced during the interval between the surveys. By becoming visual and objective, with the help of a vertical view added to the horizontal one, social studies also can become historical; photographs can be catalogued, stored, compared, duplicated, and enlarged as required, and they can give depth to current work.

Finally, evaluation can be 'built into' a programme, so as to act as a continuously readjusting mechanism, a kind of thermostat or feed back, that gives the policy-maker a progressive report on his project which shows how it is working out in practice. Starting with the appraisal of the natural and social resources of an area, the effect a programme has, say, on capital investment and the secondary effects of new activity in all the sectors of life can be evaluated in time to overhaul the initial programme so that the secondary effects are taken into account and indeed creatively incorporated in the next step. The air photographic part allows the evaluation to be carried on without interference in the ordinary daily round of the community (an

important consideration when as so frequently there is an emotional situation). It becomes a matter of routine checks, not requiring the setting up of elaborate staffs under expert supervision; it can utilize photography made for a variety of purposes and thus, in favourable circumstances, can be inexpensive. Its limitation is in what cannot be caught by the camera inside the house, or standing under a tree, or is not differentiated even by the colour film or infrared photograph. This then must be made the area of research of proper ground studies. The co-operation between a variety of ground and air personnel is one of the most interesting aspects of this entire enterprise.

Thus the sociological field-worker will use the air photograph as a sampling frame, from which he picks out the households or other units in which he is interested. Because of the calculable number of units in each stratum, the samples can, in a combined study, be much smaller without loss of accuracy in the statistical findings. Smaller samples require either a smaller number of enumerators (always scarce and always difficult to supervise in the field) or allow them longer time for interviews so that they can establish better rapport with the primary informants. Better selection, better training, less time wasted in the field work by better planning of the sample, are further recommendations, particularly in under-developed countries. If in the past not more use has been made of combined air–social studies, the reasons are to be found (a) in the traditional separation of social and engineering research. In most countries air photography is associated with mapping and engineering services. (b) Air surveys are expensive and multiple uses must be found before it is feasible to marry them to social studies. (c) Before two different techniques can be happily joined their limitations and possibilities must be explored separately. With the Second World War, air photography came of age. New optical discoveries made since, which record with greater precision and more and more independently of weather conditions, as well as electronic computing devices, have taken photogrammetry far beyond the frontiers it occupied in 1945. Claims of being able to photograph an entire continent by four jet planes equipped with

new radar instruments were recently made by the Secretary for Air. In the field of social analysis, national incomes studies, anthropology, and demography, partly responding to the United Nations and its Specialized Agencies and their demand for comparative, world-wide statistical information, partly under the impress of political movements all over the world for better living standards, planning, and reconstruction, equally enormous strides have been made in survey methodology and in the use of electronic computers in cross-tabulating results.

A NEW SUB-DISCIPLINE AND ITS FURTHER EVOLUTION

The combination air and social survey will become a tool more powerful than the sum of its parts. That a skilled social analyst makes fuller use of the information of the photograph than the ordinary photogrammetrist trained by people whose background is mainly topography or engineering is not surprising. That the objective, quantitative, and topological research, which the air photograph forces upon the social analyst will give him once more an eye for aesthetic matters, is immediately apparent. Somehow, shade trees, though everyone appreciates their importance in any community, are never carefully studied by social planners, who are usually too absorbed with plumbing and the location of schools. The obsolescence of a house may be balanced by a well-kept, productive garden giving joy and health, but this is rarely recorded in our questionnaire surveys. We know intuitively that a given town is a 'good town', now we shall be able to document it. Like every statistically informed social science, sociogrammetry will have to grapple with problems of scaling, ranking, and model-making of constituent weighted factors. What can be and what is observed, how observers agree, and how interpretations can be validated, will be posers that will lead to new techniques and nomenclatures. Terms like 'visible', 'identifiable', and 'distinguishable' will acquire a technical meaning. To define them, experiments made on pilots and their ability to pick up clues are as relevant as the remarkable way in which photographers have of making their

objects look like the stereotype we have of them. A recent American film of Delft looked to the Dutch photogrammetrists at the Delft International Training Centre for Aerial Survey not at all like the city they knew and were working in. A French book of photographs on London, with its strange melancholic lighting effects, appears to Londoners more like a René Clair view of Paris. Not all that is visible is correctly identified, even by the most seasoned interpreter. It is difficult, as experiments on racial characteristics have shown, to tutor interpreters to abandon their fixed ideas of how a group 'should' look. In the familiar analysis of x-rays, despite much research, experience best reveals which cases have contracted tuberculosis and which have not.

Finally, machine aids exist – unfortunately still at forbidding costs – that map, count, and evaluate photographs; radar and television scanning devices may allow us to skip the photographic stage and convert the light impulses directly into tape recordings that can be handled by computers; infrared photographs show us not only the number of planes on an airfield but also the number that have taken-off within the last hour from a runway; the use of colour, of recording apparatus of non-image making activities (all electrical waves for instance) – the very profusion of modern possibilities will encourage research and further specialization within a new sub-discipline.

As new sociogrammetric studies open up, it may be well to remember, however, that they are but a systematical, instrument-aided, endeavour of what appears to be a natural proclivity of the mind. The child, with godlike eye, paints the table from above, knowing it to be round, not as he *sees* it, as an oval shape. In a telling observation in what must be the first book of air archaeological pictures, Gustav Dahlmann, the author of *Hundert deutsche Fliegerbilder aus Palestina*, taken in 1917, says that the old landscape painters 'never reproduced what and how they saw, but aimed to give an oblique impression, a bird's eye view, and so far back as the sixth century in the Madaba mosaic'. Bernard of Breydenbach, the first artist to attempt a pictorial representation of the Holy Land, gave us in 1483 an

aerial view such as he himself could never have seen. Two hundred years later, despite all his new-found realism, Cornelius de Bruyn pushed Bethlehem and Jerusalem into one picture. Air–social science only extends an ancient conviction that great knowledge is possessed by anyone who looks down on our Earth and its people from the skies.

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RESEARCH REPORT

A. W. HASLETT

PHOTOELECTRIC ASTRONOMY

THE photographic plate – for some three generations the primary recording device used by astronomers – is beginning to give way to photoelectric devices. Photocells have for some time been the best way of measuring both the apparent brightness, or magnitude, of stars and also their colour index. Their greater sensitivity now makes it probable that photoelectric devices of one kind or another will take the place of the photographic plate as the primary means of recording spectra.

Two methods are available, of which one has already a discovery to its credit. This is the electronic camera developed by Professor A. Lallemand and his colleagues at the Paris Observatory. It is about as simple in principle as it could be, but suffers from the limitation that it involves so difficult a technique in practice that only Professor Lallemand appears to be able to make it work. Giving the discovery first, it has been used in conjunction with the 120-inch telescope of the Lick Observatory of the University of California to measure spectral shifts shown by individual stars in the central region of the Andromeda Nebula. Spectrograms were obtained in exposures of from 15 to 45 minutes each, whereas with the same telescope and spectrograph photographic exposures of from 5 to 15 hours would have been necessary. These measurements have led to the surprising conclusion that stars in the central region of the nebula are moving at speeds consistent with their making one revolution about the centre every million years – one hundred times as fast as the rate of rotation found earlier for stars in the outer part of the nebula.

The principle of Professor Lallemand's arrangement is that electrons ejected from a photocathode are accelerated to an

energy of some 20 keV and are then focused on to an electron-sensitive emulsion. An objection to the method is that vapours, emitted under vacuum conditions from the emulsion, quickly 'poison' the photocathode. Professor Lallemand's solution is to give the photocathode a clean start by processing it inside a sealed envelope, and for the rest to rely on continuous refrigeration to reduce the rate of vapour emission from the emulsion; but his procedures are probably too difficult to be adopted for routine use in observatories.

An alternative approach is to use some form of image intensifier. One such device was developed some years ago in the Soviet Union. Its performance appeared promising, but there has been no experience of it in other countries. Another has been developed lately by W. L. Wilcock and D. L. Emberson in the Department of Instrument Technology at the Imperial College of Science. Their device consists of a photocathode, five stages of electron multiplication at thin films, followed by focusing of the electrons from the last film on to a fluorescent screen. With this arrangement a light multiplication of 50,000 has been secured, starting from individual photons. The tubes that have been made so far can handle images of up to 1 cm square in size, and give a resolution of 1/15th mm. This means that as much detail can be transmitted in any one picture as is given by 250-line television.

In this form of intensifier, the electron multiplying material is potassium chloride, and the practical difficulty has been to arrive at a means of support that would withstand the process of baking-out necessary in any form of high-vacuum device. The supporting material adopted is a thin film of aluminium oxide, half a millionth of an inch thick. Th : includes a sufficient layer of metallic aluminium to provide a conducting path needed to neutralize the electric charge that would otherwise build up from the fact that some five times as many electrons are emitted on one side of the film as impinge on the other. Building bigger tubes will imply making bigger thin films. This is clearly one way – and the most obvious one – by which more details could be transmitted. Another possibility is to make use

of the high potential speed of such a system – a millionth of a second is enough, in principle, for a single process of intensification – and to view the image in sections. As well as astronomy, the device has possible applications in nuclear physics, in conjunction with the scintillation method of observing the tracks of charged particles, and in radiology as a solution to the problem of obtaining medical X-rays with only a fraction of the dose now necessary.

UNSEEN SIDE OF THE MOON

The first – apparently composite – Russian photograph of the hitherto unseen side of the Moon has been so widely published and discussed that the stage of initial surprise and admiration may be supposed by this time to be over. The technique of photography, automatic processing, and picture transmission which they have developed imply space vehicles of a size that only the Russians could now launch; while control of the aspect of the space vehicle during photography appears to have involved a combination of devices, including direction sensing, corrective jets, electronic control, and gyroscopic stabilization. For the present, therefore, it seems that the Russians – and only the Russians – will be in a position to clear up the most obvious question raised by their own picture: whether the comparative scarcity of well-marked features on the hitherto unseen side of the Moon should be accepted as genuine. They have gone out of their way to suggest that it is. They can supply decisive proof just as soon as they can place a vehicle, similarly equipped, into orbit about the Moon, so enabling all aspects of the Moon to be observed under comparable conditions during the course of 28 days. While this is a considerably more exacting requirement than their already astonishing performance, it is the only way of meeting the condition that, when proceeding from one observation to another, there should be a direct comparison of results using the two methods – in this case, conventional photography of the known side of the Moon as viewed from the Earth and photographs of the same side transmitted from a space vehicle.

DIFFRACTION GRATINGS FOR MEASUREMENT

New uses for the diffraction grating in science and industry as a means of measuring position, movement, and rotation are being developed as a result of research by Dr L. A. Sayce, Superintendent of the Light Division of the National Physical Laboratory, Teddington. At the same time, the methods of making diffraction gratings in quantity which were initiated some years ago by Sir Thomas Merton are being improved and extended, and there seems to be no reason in principle why gratings of 'perfect' regularity – i.e., without detectable irregularity – should not be arrived at by stages.

The idea of using diffraction gratings as rulers originated at the N.P.L. as a new line of thought suggested by their more ready availability. An obvious obstacle – that scale markings, spaced at some thousands of lines per inch cannot be distinguished by eye – is not necessarily a limitation; means of observation had been provided in advance by an observation made by Lord Rayleigh. An easy – and, as is now clear, an extremely flexible – solution is available in the patterns of light and dark bands, known as moiré fringes, so-called from their appearance on moiré silk, in which there are two overlapping layers of fabric. In the same way, when two transparent gratings are placed on top of one another, with their lines nearly parallel, but not quite, moiré fringes are formed in a direction at right angles to the grating lines. The theory of such fringes has been worked out by J. Guild of the Light Division in a form that takes account of the close spacing of grating lines, and further types of pattern have been investigated. For example, moiré fringes are formed also between gratings cut radially on circular discs. In either case, displacement or rate of movement can be measured by forming fringes between a fixed and a moving grating, and the scale of the fringes can be adjusted at will by changing the relative disposition of the gratings. Moreover, the fringes represent an averaged measurement, based on the relative positions of a large number of grating lines, so that local errors are eliminated.

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DIFFRACTION GRATINGS FOR MEASUREMENT

New uses for the diffraction grating in science and industry as a means of measuring position, movement, and rotation are being developed as a result of research by Dr L. A. Sayce, Superintendent of the Light Division of the National Physical Laboratory, Teddington. At the same time, the methods of making diffraction gratings in quantity which were initiated some years ago by Sir Thomas Merton are being improved and extended, and there seems to be no reason in principle why gratings of 'perfect' regularity – i.e., without detectable irregularity – should not be arrived at by stages.

The idea of using diffraction gratings as rulers originated at the N.P.L. as a new line of thought suggested by their more ready availability. An obvious obstacle – that scale markings, spaced at some thousands of lines per inch cannot be distinguished by eye – is not necessarily a limitation; means of observation had been provided in advance by an observation made by Lord Rayleigh. An easy – and, as is now clear, an extremely flexible – solution is available in the patterns of light and dark bands, known as moiré fringes, so-called from their appearance on moiré silk, in which there are two overlapping layers of fabric. In the same way, when two transparent gratings are placed on top of one another, with their lines nearly parallel, but not quite, moiré fringes are formed in a direction at right angles to the grating lines. The theory of such fringes has been worked out by J. Guild of the Light Division in a form that takes account of the close spacing of grating lines, and further types of pattern have been investigated. For example, moiré fringes are formed also between gratings cut radially on circular discs. In either case, displacement or rate of movement can be measured by forming fringes between a fixed and a moving grating, and the scale of the fringes can be adjusted at will by changing the relative disposition of the gratings. Moreover, the fringes represent an averaged measurement, based on the relative positions of a large number of grating lines, so that local errors are eliminated.

By using fringes of both kinds – the type corresponding with a rule and the radial type – a movement of translation can be compared continuously with one of rotation. This means that the movement of, for example, a lathe can be servo-controlled to a high degree of precision. In order to do this, both sets of fringes are converted by photocells into electrical oscillations. The scales of the two sets of fringes can be adjusted so that, in the intended conditions of operating, their respective frequencies are the same. These frequencies are then compared electronically, and any difference between them is used to operate a servo mechanism controlling one or other movement. In this way, a lathe at the N.P.L. with an intrinsic accuracy of one ten-thousandth of an inch has been controlled to an accuracy better than a millionth of an inch. In the same way, a lathe with an intrinsic accuracy of a thousandth of an inch, or worse, could be controlled to give a better performance than the best previously existing lathe. While there are other possible faults in a lathe which cannot be eliminated in this way, it looks as if it may be more economic in the long run to allow somewhat greater tolerances than have been accepted hitherto for the best lathes, and to attain whatever accuracy may be required by the grating system of control. Another possibility opened up by the method is that of obtaining gear systems of almost perfect precision. This should be worth while in at least two cases: in precision instruments and in the transmission systems of marine engines, where a comparatively small saving in fuel justifies any reasonable trouble in getting it. Finally, there is an already more familiar use of diffraction gratings in the Ferranti system of programmed operation of machine tools, to direct accurately the position of the cutting tool in a milling-machine.

On the other part of the story – the improvement of diffraction gratings – it may be recalled that Sir Thomas Merton's method of producing gratings in quantity depends on ruling in the first place neither on a flat surface nor a convex mirror, as formerly, but on a cylinder. In order to do this, he used a special lathe of the kind employed to cut screws, but geared down so as to turn at an extremely slow speed. In order to

correct for imperfections in the lathe, he made use of the elas-
ticity of cork to copy the fine screw, already cut on one cylinder,
on to a second cylinder in line with the first, but with imperfec-
tions now averaged out. Thirdly, he arrived at a method for
producing flat, glass-backed copies, made from a gelatine
mounting. Sir Thomas Merton's cork has now been replaced by
an arrangement using pith and springs, and there is available
an optical method, as well as the mechanical one, by which
residual irregularities in gratings can be progressively removed,
until a point is reached when no further irregularity can be
detected.

ULTRA-VIOLET 'FURNACES'

A new use of solar energy – to bring about photochemical
reactions on a semi-industrial scale by concentrating the ultra-
violet radiation of sunlight on to a reaction chamber under
controlled conditions of temperature – is being studied at the
Laboratoire La Bouzareah, just outside Algiers, of the French
Centre National pour la Recherche Scientifique. An experi-
mental paraboloid of 8·4 metres diameter, fully steerable like
a telescope, is being used in research on reactions thought to
be promising and on different types of reaction chamber. The
idea behind the research is that, either in the Atlas Mountains,
with the advantage of altitude, or on the northern fringe of
the Sahara, with longer power of sunlight, it may be practical
to make products for which local markets exist.

Two reaction systems have been studied. One which needs a
high temperature – about 3,000° C has been found best – is the
formation of a mixture of nitrogen oxides from the nitrogen
and oxygen of the air, with nitric acid as the final product. For
the purpose of this reaction, 2·3 square metres of mirror is
equivalent to 60 kW of electric power, using the Birkland arc
process. The second reaction is the chlorination of benzene to
give benzene hexachloride, for use as an insecticide. This re-
quires a low temperature – not more than 130° C – and an inter-
vening layer of water is used to absorb infra-red radiation.
Various further projects are being considered – the view taken

in the laboratory being that the method can be made economic in the conditions envisaged, although no attempt to arrive at accurate costs for a larger, production type of furnace has yet been made.

UNNATURAL AMINO ACIDS

I am indebted to Mr H. D. Tunstall Pedoe for calling attention to the fact that in *Science News 52* (p. 118), under this heading, the *un*natural amino acids were said, incorrectly, to be the *laevo* forms. It is the 'natural' amino acids that are *laevo*.

SOME BOOKS RECEIVED

A HISTORY OF WESTERN TECHNOLOGY by Friedrich
Klemm, translated by Dorothea Waley Singer (London, Allen
and Unwin, 1959), pp. 401, 32s.

MAN THE MAKER - A HISTORY OF TECHNOLOGY AND
ENGINEERING by R. J. Forbes (London, Constable, 1958),
pp. 363, 30s.

No one has a more encyclopedic knowledge of the history of
technology than Professor Forbes, but the very vastness of his learn-
ing brings its dangers. That he can paint the broad canvas of techno-
logical development, there is no doubt, but he is prone to error in
small, but nevertheless important, details. To take an example, the
Christian names of his characters, Dudley, Davy, and Dundonald,
are all given incorrectly at various places – and there are other slips
that cannot be dealt with in such a short note as this. So – for the
broad sweeps, useful; for the detail, to be used with caution.

Dr Klemm's history takes the form of quotations from contem-
porary writings which reveal the causes of technological progress,
epoch by epoch. These are related to the relevant intellectual forces,
and their mutual interaction is discussed. The texts selected range
from the philosophies of classical antiquity to automatic factories
as seen by Norbert Wiener. Several attempts have been made to do
this before, but they have confined themselves to rather narrower
fields. But technology is life, and we have here, presented as thought
fit and proper by those involved, the immense sweep of human
endeavour over two millennia.

APPARATUS AND METHODS OF OCEANOGRAPHY – Part
One : Chemical by H. Barnes (London, Allen and Unwin,
1959), pp. 341, 40s.

Dr Barnes's earlier volume, Oceanography and Marine Biology,
was reviewed in Science News 52. Now he has embarked on the pro-
duction of a more ambitious work sponsored by the Union Géo-
désique et Géophysique Internationale. The volume deals with the
chemical side of oceanographic problems. The author has borne in

mind the fact that many institutes still only have limited facilities, but by drawing attention to the existence of more sophisticated methods he suggests that rewarding prizes await their introduction. If the laboratories that are lagging can be induced to take up the more productive lines, here is the text-book to help them in their expansion.

A SHORT HISTORY OF SCIENTIFIC IDEAS TO 1900 by Charles Singer (Oxford, Clarendon Press, 1959), pp. 525, 35s.

We are fortunate that, having got his vast *History of Technology* out of the way, Dr Charles Singer, now more than eighty years young, has found the time and the energy to revise some of his earlier works. These pioneer studies, perhaps more than any other publications in the English language, have created the present healthy and growing interest in the history and philosophy of science and of technology. This volume is a rewritten, enlarged, and much more fully illustrated edition of *A Short History of Science* which was published in 1941, in the rewriting of which Dr Singer has been assisted by other historians, Professor Dingle, Dr Derek Price, and Dr Angus Armitage. While Dr Singer is still given as the author on the title page, the new collaboration has helped to give a better perspective particularly on the physical side, the previous bias having been somewhat biological – Dr Singer himself approached the history of science through a professional training in medicine.

The history of science is now such a vast subject that any reviewer can lament that his own particular interests appear to have received less consideration than he considers they merit. The present reviewer's main complaint would be that four-fifths of the text precede Darwin and Pasteur, even allowing that the volume has been renamed *A Short History of Scientific Ideas to 1900*. Nevertheless, over the period it covers, there is no doubt that this new edition will help to keep this important study in its existing position of the standard work on the subject for years to come.

THE LOGIC OF SCIENTIFIC DISCOVERY by Karl R. Popper (London, Hutchinson, 1959), pp. 480, 50s.

This is the long-expected English translation of Popper's classic *Logik der Forschung* published in Vienna nearly a quarter of a century ago. For the English edition, however, the author, who is

now professor of Logic and Scientific Method at the London School of Economics, has added many footnotes to his text, and new appendixes amounting to about half the length of the original work. Thus, not only is this important work available to readers who find that they cannot cope with the philosophy of science in any language other than their own, but the author has attempted to clear up points of obscurity in the original text. In spite of this help, we still have a contribution to learning that calls for the closest study if full benefit is to be derived from it. A further contribution from the author, *Postscript: After Twenty Years*, is promised by the publishers.

OUTLINE OF HUMAN GENETICS by L. S. Penrose (London, Heinemann, 1959), pp. 146, 12s 6d.

Many current volumes on scientific topics start their lives with the twin disadvantages of excessive length and high cost. Professor Penrose's study suffers from neither. Its price is modest, and in less than 150 pages he presents in a clear and lively manner the salient points of human genetics as understood today. There may have been a time when genetics seemed a remote and ivory-tower topic – albeit Mendel's classic work was done on culinary rather than decorative peas – but the trend of world events in recent years has brought genetics into the forefront of current political thinking – radiation hazards, the colour question, artificial insemination, eugenics, and the suspected decline in intelligence. To form some sort of intelligent opinion on these matters, the citizen of 1960 must have some acquaintance with genetic principles. To acquire them quickly but accurately in a harassed world, here is the book for him.

DARWIN AND THE DARWINIAN REVOLUTION by Gertrude Himmelfarb (London, Chatto and Windus, 1959), pp. 422, 42s.

The centenary of the Darwin-Wallace communication to the Linnean Society and the publication of the *Origin of Species* some sixteen months later have occasioned a veritable spate of Darwiniana. Dr Himmelfarb's is not the least of these stimulated works. This long and well-annotated biography is better on the whole on the social and intellectual climate of Darwin's endeavours than on his contribution to scientific thought, but, nevertheless, it throws some interesting fresh light on Darwin and Darwinism.

ALAN M. TURING by Sara Turing (Cambridge, Heffer, 1959), pp. 157, 21s.

Within the reviewer's knowledge, this is a biography without parallel, being written by a mother about a son whose untimely death in circumstances fraught with mystery cut off one of Britain's most distinguished thinkers of recent times.

The word genius is frequently used in connexion with Alan Turing, and there is little doubt that he indeed had a mind of great originality. How he met his death will forever remain a mystery – that the official verdict was suicide is really beside the point. But what one is struck by in this sincere and unselfconscious biography is the difficulties that the possessor of such a mind, and those whom fate has decreed as its nurturers, have to face in bringing it to fruition.

Alan Turing had more than his share of good fortune in this connexion. On both sides his ancestry contained names of distinction; despite the buffeting that the child of parents whose life was divided between India and England is bound to suffer, *rapport* between child and parents, particularly the mother, seems to have been satisfactory; in the biography, his school (Sherborne) comes in for considerable praise, yet Turing's life, if we accept the verdict, was somehow incomplete and maladjusted.

Genius is infinitely precious. Here is indeed a problem. We have no knowledge of how to produce it: are we even fitted to cultivate it to our full advantage when nature thrusts it upon us. Turing's death returns a mocking answer – no. Perhaps some of those who read this moving story, not for what it is, but for what it implies, will come to realize that here is a problem worthy of study at the highest level.

A GUIDE TO FRESHWATER INVERTEBRATE ANIMALS by T. T. Macan (London, Longmans, 1959), pp. 118, 11s 6d.

The aim behind this short guide to freshwater invertebrates is to provide the field naturalist, be he sixth-former or university student, with sufficient data to identify his specimen to the nearest group, usually the family. This is as much as can be expected from a small guide, but the enthusiastic seeker for information can take his researches further by using the extensive references to more specialized work through which the species may be identified.

A most attractive feature of the volume is the 200 illustrations, many of them specially drawn for this work.

SCIENCE IN INDUSTRY – POLICY FOR PROGRESS by C. F. Carter and B. R. Williams (London, Oxford University Press, 1959), pp. 186, 21s.

This is the third and final report of the Science and Industry Committee which, sponsored by the British Association for the Advancement of Science, the Royal Society of Arts, and the Nuffield Foundation, has for several years been investigating the factors that influence the adoption of new scientific ideas by British industry. The two earlier reports gave the Committee's conclusions on the facts: they were published in 1957 and 1958. The present report gives specific proposals on the one hand to industry itself, and on the other to the Government on the policy and action that are required to secure the fruitful application of science to industry. It is based, in the main, on evidence given to the Committee by some 250 companies of all sizes and degrees of progressiveness.

Among the points worthy of mention are the set of general rules put forward by the authors for deciding which kinds of research and development work are likely to be most worth while, and for making use of the new ideas developed. A chapter on the communication of ideas suggests ways to make sure that new ideas are quickly picked up and appreciated. The authors set out a standard procedure for doing this which should help managements to avoid overlooking ways in which the firm can be kept fully open to new ideas. A number of proposals are made on technical and scientific education, with the suggestion thrown out that perhaps technical training is falling behind the training of technologists and scientists. A useful feature of the volume is a twelve-page summary for those who wish to find their way quickly to the main suggestions for action.

It will be up to the new Minister of Science to consider most of the problems discussed in the second half of the report. The authors say bluntly that 'we doubt if it can be said that a Government policy on the application of science really exists'. Few will doubt this, but the facts on which such a policy should be based have now been laid open.

ABOUT OUR CONTRIBUTORS

S. A. BARNETT does research on social behaviour and 'social stress' in wild rats; he also breeds mice at minus 3° C, and studies the effects of low temperature on their breeding and growth. He is also working on hybrid vigour and resistance to cold. At Glasgow University he is a senior lecturer in Zoology.

W. A. BELL was educated at Dundee High School and the University of St Andrews, where he graduated in 1938. During the war he worked on the Atom Bomb Project, on the production of heavy water, and also on various aspects of the separation, of the isotopes of uranium by diffusion. After the war he returned to Queen's College, Dundee, University of St Andrews, and completed research on acid and basic catalysis, for which he was awarded the degree of Ph.D. Following a short period as a demonstrator, in 1949 he joined the staff of the British Jute Trade Research Association, where, at present, he is head of the Chemistry Department.

J. E. PAGE was educated at Newport High School and at Cardiff University and Technical Colleges. He is a member of the research staff of Glaxo Laboratories and has specialized in the application of physical methods, such as polarography, radioactive isotopes, and infra-red spectroscopy, to organic and biochemical problems. In 1938 he was awarded the Ph.D. and in 1957 the D.Sc. degree of London University.

G. L. ROGERS was educated at Berkhamsted School and the Science Museum, South Kensington. Later he went to Emmanuel College, Cambridge, and during the war taught Physics at the Cavendish Laboratory. He spent the years 1946–51 at Dundee, and 1952–6 at Wellington, New Zealand. Since 1957 he has been at the College of Advanced Technology, Birmingham. His research interests include optics, moiré patterns, and the techniques of teaching and administration. Hobbies: writing, photography, and stereoscopy.

A. H. ROSE, who is 29, is a lecturer in microbiology at Heriot-Watt College in Edinburgh. He is a graduate of Birmingham University, where he obtained a First Class Honours B.Sc. in Industrial Fermentation in 1950, and a Ph.D. in Applied Biochemistry in 1954. Prior to taking up his present appointment in 1958, he served as a National Service Education Officer in the Royal Air Force, and held a King George VI Memorial Fellowship at Rutgers University in New Jersey and a Fellowship studying mould fermentations

at the National Research Council of Canada in Ottawa. Dr Rose's research interests include the role of biotin in yeast metabolism and the biochemistry of psychrophilic micro-organisms. He has previously contributed to *Science News 43*.

L. C. ROSELAAR was born in 1930 and was educated at Tottenham County School and St Catherine's Society, Oxford. After National Service as an education officer in the Royal Air Force, he was engaged in research in combustion chemistry at the Royal College of Science, London, where he obtained his Ph.D. in 1957. He is now a lecturer in Physical Chemistry at South-East Essex Technical College.

L. SILBERMAN, Visiting Associate Professor at the University of Chicago and member of the Center for Economic Growth and Cultural Change, has been a university teacher since 1943. He is happiest 'in the field' as part of a commission or researching on labour, housing, town-planning, or social welfare problems in Africa – his chosen field. Latterly he has been experimenting with new devices for collecting social information for policy planning. Some of his books are: *Nairobi Master Plan* (co-author); *Planning and Welfare in Colonies*; *Analysis of Society, Class, and Colour in Six Schools* (co-author); *Community Planning* (co-author); and *Population Problems* (co-author).

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